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<b>(54) Title:</b> CATALYST SYSTEMS FOR REDUCTION OF OXIDES OF NITROGEN		
<b>(57) Abstract</b> <p>A catalyst system for reduction of oxides of nitrogen is described comprising aluminium oxide and at least one metal oxide which is different to aluminium oxide. Also disclosed is an automotive exhaust catalyst system for reducing oxides of nitrogen comprising an automotive exhaust catalyst system support together with the catalyst system of the invention, a catalyst system for reducing oxides of nitrogen from combustion sources comprising a catalyst system support together with the catalyst system of the invention, a method of preparing a catalyst system, a method of preparing an automotive catalyst system, a process for removing oxides of nitrogen from exhaust gas from a combustion source and a process for removing oxides of nitrogen from exhaust gas from a combustion source.</p>		

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## **Catalyst Systems for Reduction of Oxides of Nitrogen**

### **Field of the Invention**

This invention relates generally to the field of reduction of oxides of nitrogen ("NO<sub>x</sub>") from mobile and stationary emission sources, and more particularly to a catalyst for the reduction of NO<sub>x</sub> emissions and process for making same. This invention also relates to a process for reduction of oxides of nitrogen, catalyst systems, automotive catalyst systems and an apparatus for reducing oxides of nitrogen.

### **Background of the Invention**

In recent years environmental regulations have decreed that emissions of the oxides of nitrogen which arise from both mobile and stationary combustion processes, must be strictly regulated. Consequently, substantial research has been directed towards the discovery of a suitable catalytic system to facilitate the reduction of NO<sub>x</sub> to nitrogen.

Therefore, there exists a definite need to discover means by which to improve the catalytic performance of alumina based deNO<sub>x</sub> catalysts.

A typical object of the invention is reduction of NO<sub>x</sub> present in lean burn engine exhausts. Another typical object of the invention is reduction of NO<sub>x</sub> emitted from diesel engines. Another typical object of the invention is reduction of NO<sub>x</sub> from stationary combustion sources. A further typical object of the invention is reduction of NO<sub>x</sub> from natural gas fuelled vehicles. Yet another typical object of the invention is ability to use methane as a reductant.

Still yet another typical object of the invention is ability to use alcohols and aldehydes as reductants. Another typical object of the invention is ability to use higher hydrocarbons as reductants. Another typical object of the invention is resistance to thermal degradation. A further typical object of the invention is resistance to deactivation by water at elevated temperatures. Yet another typical object of the invention is resistance to poisoning by oxides of sulfur.

Other objects and advantages of the present invention will become apparent from the following description, taken in connection with the accompanying drawings.

### **Summary of the Invention**

According to a first embodiment of this invention, there is provided a catalyst system for reduction of oxides of nitrogen comprising:

- a) aluminium oxide; and
- b) at least one metal oxide which is different to aluminium oxide.

According to a second embodiment of this invention, there is provided a catalyst system for reduction of oxides of nitrogen comprising:

- a) aluminium oxide; and
- b) boron oxide.

According to a third embodiment of this invention, there is provided a catalyst system for reduction of oxides of nitrogen comprising:

- 5 a) aluminium oxide; and
- b) gallium oxide.

According to a fourth embodiment of this invention, there is provided a catalyst system for reduction of oxides of nitrogen comprising:

- a) aluminium oxide; and
- 10 b) a mixture of boron oxide and gallium oxide.

According to a fifth embodiment of this invention, there is provided a catalyst system for reduction of oxides of nitrogen comprising:

- a) aluminium oxide;
- b) at least one metal oxide which is different to aluminium oxide; and
- 15 c) a promoting agent

According to a sixth embodiment of this invention, there is provided a catalyst system for reduction of oxides of nitrogen comprising:

- a) aluminium oxide
- b) gallium oxide; and
- 20 c) a promoting agent.

According to a seventh embodiment of this invention, there is provided a catalyst system for reduction of oxides of nitrogen comprising:

- a) aluminium oxide;
- b) gallium oxide; and
- 25 c) a promoting agent selected from the group of a noble metal, alkaline earth metal, rare earth element, an element of group 4A in the periodic table, an element of group 5A in the periodic table.

According to an eighth embodiment of this invention, there is provided a catalyst system for reduction of oxides of nitrogen comprising:

- 30 a) aluminium oxide
- b) a mixture of gallium oxide and boron oxide; and
- c) a promoting agent.

According to a ninth embodiment of this invention, there is provided a catalyst system for reduction of oxides of nitrogen comprising:

- 35 a) aluminium oxide;

b) a mixture of gallium oxide and boron oxide ;and

c) a promoting agent selected from the group of a noble metal, alkaline earth metal, rare earth element, an element of group 4A in the periodic table, an element of group 5A in the periodic table.

5 According to a tenth embodiment of this invention, there is provided a catalyst system for reduction of oxides of nitrogen comprising:

a) aluminium oxide;

b) boron oxide; and

c) a promoting agent.

10 According to an eleventh embodiment of this invention, there is provided a catalyst system for reduction of oxides of nitrogen comprising:

a) aluminium oxide;

b) boron oxide; and

c) a promoting agent selected from the group of a noble metal, alkaline earth  
15 metal, rare earth element, an element of group 4A in the periodic table, an element of group 5A in the periodic table

According to a twelfth embodiment of this invention, there is provided a catalyst system for reduction of oxides of nitrogen comprising:

a) aluminium oxide; and

20 b) 1 to 50 % gallium oxide

c) a promoting agent selected from the group of a noble metal, alkaline earth metal, rare earth element, an element of group 4A in the periodic table, an element of group 5A in the periodic table.

25 According to a thirteenth embodiment of this invention, there is provided a catalyst system for reduction of oxides of nitrogen comprising:

a) aluminium oxide

b) 1 to 25 % gallium oxide; and

c) a promoting agent selected from the group of a noble metal, alkaline earth  
30 metal, rare earth element, an element of group 4A in the periodic table, an element of group 5A in the periodic table.

According to a fourteenth embodiment of this invention, there is provided an automotive exhaust catalyst system for reducing oxides of nitrogen comprising a support for a catalyst system together with the catalyst system of any one of the first to thirteenth embodiments of this invention.

According to a fifteenth embodiment of this invention, there is provided a catalyst system for reducing oxides of nitrogen from combustion sources comprising a support for a catalyst system together with the catalyst system of any one of the first to thirteenth embodiments of this invention.

5 According to a sixteenth embodiment of this invention, there is provided a method of preparation of a catalyst system comprising:

a) mixing a precursor of aluminium oxide and a precursor of a metal oxide which is different to aluminium oxide;

b) adding a basic compound;

10 c) drying and heating the resulting mixture;

so as to form a catalytic system for reduction of oxides of nitrogen.

According to a seventeenth embodiment of this invention, there is provided a method of preparation of a catalyst system comprising:

a) mixing a precursor of aluminium oxide and a precursor of gallium oxide;

15 b) adding a basic compound;

c) drying and heating the resulting mixture;

According to an eighteenth embodiment of this invention, there is provided a method of preparation of an automotive catalyst system comprising:

20 a) mixing a precursor of aluminium oxide and a precursor of gallium and/or a boron oxide ;

b) adding a basic compound;

c) drying and heating the resulting mixture;

d) forming a catalytic system for reduction of oxides of nitrogen; and

e) impregnating said catalytic system on a support material.

25 According to a nineteenth embodiment of this invention, there is provided a process for removing oxides of nitrogen from exhaust gas from a combustion source comprising:

a) impregnating a catalyst support with aluminium oxide and a gallium and/or a boron oxide;

30 b) treating the catalyst support with a reductant selected from the group of a hydrocarbon, aldehyde or alcohol; and

c) directing exhaust gas containing oxides of nitrogen over the impregnated catalyst support;

35 According to a twentieth embodiment of this invention, there is provided a process for selectively removing oxides of nitrogen from exhaust gas from a combustion source comprising:

a) impregnating a catalyst support with aluminium oxide and a gallium and/or a boron oxide;

b) treating the catalyst support with a reductant selected from the group of a propene or methane;

5 c) directing exhaust gas containing oxides of nitrogen over the impregnated catalyst support;

According to a twenty first embodiment of this invention, there is provided an apparatus for reducing oxides of nitrogen in exhaust gas comprising:

a) an inlet for the introduction of exhaust gas ;

10 b) a housing connected to said inlet for exhaust gas;

c) an outlet for the exhaust gas to be released into the surrounding atmosphere;

wherein the housing b) further comprises a catalyst system of any one of the first to thirteenth embodiments of this invention.

Other embodiments of the invention include:

15 (1) An automotive exhaust catalyst system for reducing oxides of nitrogen comprising an automotive exhaust catalyst system support together with the catalyst system of the invention.

(2) A catalyst system for reducing oxides of nitrogen from combustion sources comprising a catalyst system support together with the catalyst system of the invention.

20 (3) A method of preparing a catalyst system comprising:

a) mixing a precursor of aluminium oxide and a precursor of a metal oxide which is different to aluminium oxide;

b) adding a basic compound;

c) drying and heating the resulting mixture;

25 so as to form a catalytic system for reduction of oxides of nitrogen.

(4) A process for removing oxides of nitrogen from exhaust gas from a combustion source comprising:

a) impregnating a catalyst support with aluminium oxide and at least one metal oxide is selected from the group consisting of boron oxide, gallium oxide and a mixture  
30 of boron oxide and gallium oxide;

b) directing a reductant and exhaust gas containing oxides of nitrogen over the impregnated catalyst support whereby the oxides of nitrogen in said gas are reduced.

(5) A process for removing oxides of nitrogen from exhaust gas from a combustion source comprising:

directing a reductant and the exhaust gas containing oxides of nitrogen over the a catalyst system of the invention whereby the oxides of nitrogen in said gas are reduced.

(6) A process for removing oxides of nitrogen from exhaust gas from a combustion source comprising:

- 5 directing a reductant and exhaust gas containing oxides of nitrogen over the a catalyst support impregnated with a catalyst system of the invention whereby the oxides of nitrogen in said gas are reduced.

The processes for removing oxides of nitrogen are typically carried out under the following reaction conditions:

- 10 (1) gas hourly space velocity of the reductant/exhaust gas (the term exhaust gas may be taken to include any gas containing oxides of nitrogen) of 0.005 to 0.30 g/min/cm<sup>3</sup> of the catalyst system, more typically 0.02 to 0.30 g/min/cm<sup>3</sup> of the catalyst system. More typically, the gas hourly space velocity (GHSV) is in the range of 50,000 to 250,000h<sup>-1</sup>, 80,000 to 200,000h<sup>-1</sup>, 100,000h<sup>-1</sup> to 200,000h<sup>-1</sup>, 150,000h<sup>-1</sup> to 200,000h<sup>-1</sup>, 175,000h<sup>-1</sup> to 200,000h<sup>-1</sup>, 100,000h<sup>-1</sup> to 170,000h<sup>-1</sup>, 120,000h<sup>-1</sup> to 180,000h<sup>-1</sup> or 130,000h<sup>-1</sup> to 170,000h<sup>-1</sup>;
- (2) the catalyst concentration in the catalyst system is 10 to 100% w/w. More typically, the gas hourly space velocity (GHSV) is in the range of 50,000 to 250,000h<sup>-1</sup>, 80,000 to 200,000h<sup>-1</sup>, 100,000h<sup>-1</sup> to 200,000h<sup>-1</sup>, 150,000h<sup>-1</sup> to 200,000h<sup>-1</sup>, 175,000h<sup>-1</sup> to 200,000h<sup>-1</sup>, 100,000h<sup>-1</sup> to 170,000h<sup>-1</sup>, 120,000h<sup>-1</sup> to 180,000h<sup>-1</sup> or 130,000h<sup>-1</sup> to 170,000h<sup>-1</sup>.
- (3) the molar ratio of reductant to oxides of nitrogen is typically in the range of stoichiometric to 5 times excess stoichiometric reductant:oxides of nitrogen, more typically in the range of stoichiometric to 2.5 times excess stoichiometric reductant:oxides of nitrogen and even more typically in the range of stoichiometric to 1.5 times excess stoichiometric reductant:oxides of nitrogen. A ratio of stoichiometric reductant:oxides of nitrogen may be used;
- 25 (4) Temperature in the range of 200 -800°C, 220 -750°C, 250 -700°C, 250 -650°C, 250 -600°C, 250 -550°C or 250 -500°C. Typically the temperature is 200°C, 250°C, 300, 350, 400°C, 450°C, 500°C, 550°C, 600°C, 650°C, 700°C, 750°C or 800°C.

### 30 Detailed Description of the Invention

The catalyst system typically further comprises a promoting agent which may be selected from a metal including a transition metal, alkali metal, alkaline earth metal, rare earth metal; an element of group 4A in the periodic table of elements; an element of group 5A in the periodic table of elements, or a noble metal.



The noble metal is typically selected from the group of platinum, palladium, iridium and rhodium.

Still more typically, the promoting agent is selected from a noble metal, cerium, silver, tin and tungsten. Yet still more typically, the promoting agent is selected from palladium, platinum and iridium.

The metal oxide of component b) is typically a single component and is selected from the group of boron oxide, gallium oxide, indium oxide. However, the metal oxide may also be a mixture of one or more of the aforesaid metal oxides.

The catalyst system further typically comprises:

- a) aluminium oxide; and
- b) boron oxide or gallium oxide.

Still typically, a promoting agent is further added to the components a) and b) above.

Still more typically, the catalyst system comprises either (1) an intimate mixture of gallium and aluminium oxides or a catalyst comprising of boron and aluminium oxides, or (2) a catalyst comprising of gallium and aluminium oxides promoted by the addition of a transition metal, or (3) a catalyst comprising of gallium and aluminium oxides promoted by the addition of a noble metal, or (4) a catalyst comprising of gallium and aluminium oxides promoted by the addition of an alkali metal, or (5) a catalyst comprising of gallium and aluminium oxides promoted by the addition of an alkaline earth, or (6) a catalyst comprising of gallium and aluminium oxides promoted by the addition of a rare earth element, or (7) a catalyst comprising of gallium and aluminium oxides promoted by the addition of an element of group 4A in the periodic table, or (7) a catalyst comprising of gallium and aluminium oxides promoted by the addition of an element of group 5A in the periodic table, or (8) a catalyst comprising of boron and aluminium oxides promoted by the addition of a transition metal, or (9) a catalyst comprising of boron and aluminium oxides promoted by the addition of a noble metal, or (10) a catalyst comprising of boron and aluminium oxides promoted by the addition of an alkali metal, or (11) a catalyst comprising of boron and aluminium oxides promoted by the addition of an alkaline earth, catalyst comprising of boron and aluminium oxides promoted by the addition of a rare earth element, or (12) a catalyst comprising of boron and aluminium oxides promoted by the addition of an element of group 4A in the periodic table, and (13) a catalyst comprising of boron and aluminium oxides promoted by the addition of an element of group 5A in the periodic table.

Suitable group 4A elements are Ge, Sn and Pb and mixtures thereof. Suitable group 5A elements are As, Sb and Bi and mixtures thereof.

The following Table A provides a typical weight ratio of the component a) aluminium oxide to the component b) gallium oxide and/or boron oxide of this invention in the catalyst system of this invention. Table A illustrates these values in parts by weight.

Table A

Aluminium oxide	Gallium oxide and/or Boron oxide
1	0.001, 0.002, 0.003, 0.004, 0.005, 0.006, 0.007, 0.008, 0.009, 0.01, 0.02, 0.021, 0.022, 0.023, 0.024, 0.025, 0.026, 0.027, 0.028, 0.029, 0.03, 0.031, 0.032, 0.033, 0.034, 0.035, 0.036, 0.037, 0.038, 0.039, 0.04, 0.041, 0.042, 0.043, 0.044, 0.045, 0.046, 0.047, 0.048, 0.049, 0.05, 0.051, 0.052, 0.053, 0.054, 0.055, 0.056, 0.057, 0.058, 0.059, 0.06, 0.061, 0.062, 0.063, 0.064, 0.065, 0.066, 0.067, 0.068, 0.069, 0.07, 0.08, 0.09, 0.10, 0.15, 0.20, 0.25, 0.30, 0.35, 0.40, 0.45, 0.50, 0.55, 0.60, 0.65, 0.70, 0.75, 0.80, 0.85, 0.90, 0.95, 1.0.

Still typically, the weight ratio of the component a) aluminium oxide to Gallium oxide and/or Boron oxide of this invention may be selected within the range of from 1 to 0.001 to 1 to 0.3, still more typically 1 to 0.001 to 1 to 0.25, still typically 1 to 0.001 to 1 to 0.20, still typically 1 to 0.001 to 1 to 0.15.

The following Table B provides a typical blend proportion of Aluminium oxide and Gallium oxide and/or Boron oxide under the column marked A to the promoting agent of this invention. Table B illustrates for entries numbered 1-24 the blend proportion of Gallium oxide and/or Boron oxide under the column marked A to the promoting agent in parts by weight.

Table B

Entry	A	Promoting agent
1	100	0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 1.0, 1.25, 1.5, 1.75, 2.0.
2	97.5	0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 1.0, 1.25, 1.5, 1.75, 2.0.

3	95	0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 1.0, 1.25, 1.5, 1.75, 2.0.
4	92.5	0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 1.0, 1.25, 1.5, 1.75, 2.0.
5	90	0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 1.0, 1.25, 1.5, 1.75, 2.0.
6	87.5	0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 1.0, 1.25, 1.5, 1.75, 2.0.
7	85	0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 1.0, 1.25, 1.5, 1.75, 2.0.
8	82.5	0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 1.0, 1.25, 1.5, 1.75, 2.0.
9	80	0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 1.0, 1.25, 1.5, 1.75, 2.0.
10	77.5	0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 1.0, 1.25, 1.5, 1.75, 2.0.
11	75	0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 1.0, 1.25, 1.5, 1.75, 2.0.
12	72.5	0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 1.0, 1.25, 1.5, 1.75, 2.0.
13	70	0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 1.0, 1.25, 1.5, 1.75, 2.0.
14	67.5	0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 1.0, 1.25, 1.5, 1.75, 2.0.
16	65	0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 1.0, 1.25, 1.5, 1.75, 2.0.

17	62.5	0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 1.0, 1.25, 1.5, 1.75, 2.0.
18	60	0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 1.0, 1.25, 1.5, 1.75, 2.0.
19	57.5	0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 1.0, 1.25, 1.5, 1.75, 2.0.
20	55	0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 1.0, 1.25, 1.5, 1.75, 2.0.
21	52.5	0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 1.0, 1.25, 1.5, 1.75, 2.0.
22	50	0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 1.0, 1.25, 1.5, 1.75, 2.0.
23	47.5	0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 1.0, 1.25, 1.5, 1.75, 2.0.
24	45	0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 1.0, 1.25, 1.5, 1.75, 2.0.

The typical weight percent of component a) aluminium oxide in respect of the total catalyst system composition is:

typically 1 to 99 percent by weight, further typically 25 to 99 percent by weight, still  
 5 further typically 30 to 99 percent by weight, still further typically 35 to 99 percent by weight, still further typically 40 to 99 percent by weight, still further typically 45 to 99 percent by weight, still further typically 50 to 99 percent by weight.

The typical percentage ranges of component b) gallium oxide and/or boron oxide in respect of the total composition is:

10 typically 1 to 99 percent by weight, further typically 1 to 50 percent by weight, further typically 0.1 to 50 percent by weight, still further typically 1 to 40 percent by weight, still further typically 1 to 30 percent by weight, still further typically 1 to 20 percent by weight, still further typically 1 to 15 percent by weight, still further typically 1 to 10 percent by weight, still further typically 1 to 8 percent by weight, still further typically 1

to 5 percent by weight, still further typically 1 to 3 percent by weight, still further typically 1 to 2 percent by weight. Typically component b) gallium oxide and/or boron oxide in respect of the total composition is present in an amount of 0.1, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 15, 18, 20, 25, 30, 35, 40, 45 or 50 wt%. Where gallium oxide and boron oxide are both present they are typically present in a weight ratio of gallium oxide : boron oxide in the range 0.1 : 100 to 100 : 0.1, typically 1 : 50 to 50 : 1, advantageously 1 : 25 to 25 : 1, more typically 1 : 10 to 10 : 1, even more typically 1 : 5 to 5 : 1. Where gallium oxide and boron oxide are both present they are typically present in a weight ratio of gallium oxide : boron oxide of 1 : 100, 1 : 50, 1 : 25, 1 : 10, 1 : 5, 1 : 2, 1 : 1, 2 : 1, 5 : 1, 10 : 1, 25 : 1, 50 : 1 or 100 : 1.

The typical percentage ranges of component c) promoting agent, when present, in respect of the total composition is:

typically 0.1 to 20 percent by weight, still further typically 0.1 to 15 percent by weight, still further typically 0.25 to 10 percent by weight, still further typically 0.25 to 7.5 percent by weight, still further typically 0.1 to 10 percent by weight, 0.25 to 5 percent by weight, still further typically 0.5 to 2.5 percent by weight, still further typically 0.5 to 1 percent by weight.

Typically the catalyst system has a BET surface area which is greater than the BET surface areas for gallium oxide and aluminium oxide alone. Still more typically the catalyst system has a BET surface area of 80 to 280m<sup>2</sup>/g, still more typically 90 to 270m<sup>2</sup>/g, still more typically 100 to 260m<sup>2</sup>/g, still more typically 110 to 250m<sup>2</sup>/g, still more typically 120 to 250m<sup>2</sup>/g, still more typically 130 to 250m<sup>2</sup>/g, still more typically 140 to 250m<sup>2</sup>/g, still more typically 150 to 250m<sup>2</sup>/g, still more typically 155 to 245m<sup>2</sup>/g, still more typically 165 to 245m<sup>2</sup>/g, still more typically 175 to 245m<sup>2</sup>/g, still more typically 185 to 240m<sup>2</sup>/g, still more typically 195 to 235m<sup>2</sup>/g, still more typically 200 to 235m<sup>2</sup>/g, and yet still more typically 210 to 235m<sup>2</sup>/g.

Typically, the pore size diameter of the catalyst system is less than 300 Angstroms, still typically 280 Angstroms, still typically 260 Angstroms, still more typically 250 Angstroms, still more typically 240 Angstroms, still more typically 230 Angstroms, still more typically 220 Angstroms, still more typically 210 Angstroms, still more typically 200 Angstroms, still more typically 190 angstroms, still more typically 180 Angstroms, still more typically 170 Angstroms, still more typically 160 Angstroms, still more typically, 150 Angstroms, still more typically, 140 Angstroms, still more typically 130 Angstroms, still more typically, 120 Angstroms, still more typically 110 Angstroms, still

more typically, 100 Angstroms, still more typically 90 Angstroms, still more typically, 80 Angstroms, still more typically 70 Angstroms, still more typically, 60 Angstroms, and yet still more typically the pore size diameter is less than 50 Angstroms.

Usually, reference to a precursor compound is intended to refer to a compound that  
5 when calcined in the presence of oxygen forms an oxide of the compound leaving substantially no, substantially minimal or little solid residue. The precursor is usually required to be generally soluble in the solution from which it is precipitated or coprecipitated.

Typically, the precursor of aluminium oxide is an aluminium compound which is  
10 soluble in the medium from which aluminium oxide or a precursor thereof is coprecipitated with a metal oxide or a precursor thereof which is different to aluminium oxide. The precursor may be selected from the group including aluminium nitrate, aluminium sulphate, aluminium thiocyanate, aluminium bromate, aluminium bromide, aluminium chlorate, aluminium chloride, aluminium hydroxy chloride, aluminium iodide  
15 and aluminium lactate.

Typically, the precursor of metal oxide which is different to aluminium oxide is a corresponding metal compound which is soluble in the medium in which it is dissolved with the aluminium precursor. The typical precursors of metal oxides are precursors of boron oxide and gallium oxide or a mixture thereof. Examples of the types of compounds  
20 from which the precursor of metal oxide which is different to aluminium oxide may be chosen include nitrates, oxides, carbonates, hydroxides, bicarbonates, halogens including fluorides, chlorides, bromides and iodides, urea, C<sub>1</sub>-C<sub>20</sub> carboxylates (such as for example acetates, citrates, tartrates, succinates or formates), C<sub>1</sub>-C<sub>20</sub> alkoxides and alkylamines such as ethylenediamine, diethylenediamine and triethylamine, for example. Metal nitrates and  
25 metal oxides that are soluble in the solvent from which the coprecipitation is to occur are often suitable. However, other precursors of other metal oxides such as indium oxide and/or thallium oxide are suitable. The precursor may be selected from the group including boron nitrate, gallium nitrate, boric acid, fluoroboric acid, gallium sulfate, indium chloride, indium sulfate. Where a group 4A and/or Group 5A element is required  
30 to be included an appropriate precursor of the group 4A and/or group 5A element such as a nitrate, oxide, carbonate, hydroxide, , halogen such as a fluoride, chloride, bromide or an iodide, urea, C<sub>1</sub>-C<sub>20</sub> carboxylates (such as for example acetate, citrate, tartrate, succinate or formate), C<sub>1</sub>-C<sub>20</sub> alkoxide or alkylamine.

Typically, the precursor of aluminium oxide and the precursor of metal oxide which  
35 is different to aluminium oxide are selected according to their solubility in the solution in

which the coprecipitation is to take place, the required end product and other factors relevant to the coprecipitation process such as the interaction(s) between the metal cations and the coprecipitating ions, the nature of the metal cations to be coprecipitated, the solvent, the nature of the coprecipitating reaction between the coprecipitating agent and the metal cations, the pH, the temperature etc. The precursors are suitably either initially (or are formed in situ) in the form of compounds which are soluble in the solvent from which the coprecipitation process according to the invention is to take place. The precursor compounds are chosen depending on the solvent from which the coprecipitation process is to take place, and the nature of the components in the solvent (especially the nature of the selected metal cations as well as the interaction(s) of these cations in the solvent) and the coprecipitate. Coprecipitation of a coprecipitate comprising at least two different metal cations from the solvent results from the dissolution of a coprecipitating agent in a solvent. The choice of solvent will depend on many factors including the nature of the metal cations, the interactions between the metal cations, the coprecipitating agent and the solvent, the reaction of the coprecipitating agent and the metal cations, the pH, the required temperature and the required ionic strength etc. In many instances, water is a suitable solvent. The choice of the coprecipitating agent is also dependent on many factors including the nature of the metal cations to be coprecipitated, the solvent, the nature of the coprecipitating reaction between the coprecipitating agent and the metal cations, the pH, the temperature etc. In many instances, the coprecipitating agent is suitably a dicarboxylic acid or derivatives thereof. The derivatives may include salts, esters anhydrides, amides and the like. Ammonium oxalate is one suitable derivative. Dimethyl oxalate or diethyl oxalate are also suitable. A suitable dicarboxylic acid is oxalic acid. Another suitable solution of coprecipitating ions is an aqueous solution of tartaric acid. A solution of ammonium carbonate as well as ammonia can also be used as a solution of coprecipitating ions. Also suitable as solutions of coprecipitating ions are aqueous solutions of sodium carbonate or potassium carbonate. An example of such a solution of coprecipitating ions is an aqueous solution of hydroxide and carbonate ions such as a solution of an alkylammonium hydroxide and carbonate ions together with oxalic acid or derivatives of oxalic acid. Typically, an alkaline solution of an oxalate is used as a solution of coprecipitating ions, such as an aqueous solution of sodium hydroxide or potassium hydroxide and oxalic acid or derivatives of oxalic acid. The solution of coprecipitating ions may typically include a pH adjusting agent in order that the pH can be adjusted to maximise coprecipitation. An organic solvent miscible with water can be used to make the solution of co precipitating ions. Typically organic solvents such as methanol, ethanol, propanol, butanol, pentanol, hexanol or acetone

can be used to make a solution of coprecipitating ions such as an oxalic acid solution. Generally the solution of coprecipitating ions is agitated throughout the addition procedure.

Typically, the basic compound used in the methods of the sixteenth, seventeenth and eighteenth embodiments of this invention comprises bases such as ammonia, sodium hydroxide amongst others. The addition of the basic compound is typically continued  
5 until the pH is raised to about 8 or above.

Typically, the method as described in the sixteenth, seventeenth and eighteenth embodiments of this invention as well as other coprecipitation methods described herein further comprises filtering and drying by heating the resulting coprecipitate to a  
10 temperature of between 100°C to 150°C, more typically 110°C to 130°C and still more typically 115°C to 125°C. Typically the coprecipitate is dried for a period in the range 15 minutes to 3 days, typically 30 minutes to 24 hours, and more typically 60 minutes to 12 hours.

Typically, the coprecipitate is heated at an elevated temperature typically between  
15 15°C and 1100°C degrees Celsius, 150°C and 1100°C degrees Celsius, still typically between 200°C and 1000°C and still more typically between 400°C and 700°C. The coprecipitate is usually heated to the elevated temperature so as to convert the coprecipitate to substantially an oxide catalyst by heating it to such an elevated temperature and for a sufficient time to convert the coprecipitate to a metal oxide based catalyst system. The  
20 elevated temperature and the conditions (pressure, atmosphere, time, etc.) is chosen whereby the precursors decompose so as to form a metal oxide based catalyst system.

Typically, the process of reducing oxides of nitrogen from a combustion source further comprises the addition of a promoting agent which may be selected from a metal including a transition metal, alkali metal, alkaline earth metal, rare earth metal; an  
25 element of group 4A in the periodic table of elements; an element of group 5A in the periodic table of elements, or a noble metal.

Still typically, the process of reducing oxides of nitrogen to nitrogen further comprises using hydrogen, alkanes such as methane, ethane, propane, propene, butane, alcohols such as methanol, ethanol, propanol, aldehydes, lpg gas, and higher  
30 hydrocarbons as reductants. Still more typically, methane, propane, propene, alcohols and aldehydes are used as reductants. Yet still typically methane or propene is used as the reductant.

Still more typically, the process of reducing oxides of nitrogen is used in combustion sourced emissions, still typically lean burn engine exhausts, diesel engine  
35 exhausts and natural gas vehicle exhausts.



When a catalyst support or catalyst system support is used the support typically comprises, silica, silica-alumina, titania, zirconia, alumina-silicates, alumina, activated alumina or mixtures thereof. The catalyst support or catalyst system support may be activated. The amount of catalyst or catalyst system on the support is typically in the  
5 range of 1 to 70%w/w, 5 to 60%w/w, 8 to 50%w/w, 10 to 50%w/w, 15 to 50%w/w, 20 to 50%w/w, 25 to 50%w/w or 30 to 50%w/w based on the total weight of the catalyst and support. Typically the amount of catalyst or catalyst system on the support is 15w/w, 3%w/w, 5%w/w, 7%w/w, 10%w/w, 12%w/w, 15%w/w, 18%w/w, 20%w/w, 25%w/w, 30%w/w, 35%w/w, 40%w/w, 45%w/w, 50%w/w, 55%w/w, 60%w/w or 70%w/w  
10 based on the total weight of the catalyst and support.

Gallium aluminium oxide catalysts may typically be prepared by a co-precipitation method. The source of gallium is not particularly limited, essentially any soluble gallium compound may be employed, albeit, gallium nitrate is the most convenient precursor material due to its high solubility and relative ease of supply. Likewise, the source of  
15 aluminium is not particularly limited, essentially any soluble aluminium compound may be employed, albeit, aluminium nitrate is the most convenient precursor material due to its high solubility and relative ease of supply. Synthesis of the mixed gallium-aluminium oxide is achieved by initially dissolving appropriate amounts of the gallium and aluminium precursors in an aqueous solution at a temperature typically between 0 and  
20 100°C and more typically between 20 and 80°C. Under constant agitation by a mechanical stirrer a solution of aqueous ammonia, or any other alternative base which is readily available, is added dropwise until a precipitate begins to form. Typically, the pH of the solution is raised to 8 or above. Stirring of the solution is then continued for a period extending from 1 minute to 24 hours, depending upon the precise conditions  
25 employed. Subsequently, the precipitate is filtered and then dried at 120°C for several hours.

Typically, the mixed gallium aluminium precipitate should be heated to an elevated temperature typically between 200 and 1000°C, and more typically between 400 and 700°C either in an oxygen containing atmosphere or a vacuum or in an inert gas or in a  
30 gas environment saturated with water vapour, to convert the hydroxide precipitate to an oxidic form.

Typically, the preparation of mixed boron-aluminium oxide systems may be performed in a completely analogous manner to that described for the gallium aluminium oxide system.

Typically, the gallium aluminium oxide materials may be defined by several physical properties. Firstly, it is noted that the BET surface areas of mixed gallium aluminium oxides are invariably higher than the values determined for either pure aluminium oxide or pure gallium oxide [Table 1] (for gallium loadings up to 20wt%).

5 Without wishing to be bound by theory this data may indicate that a true mixed gallium aluminium oxide phase is being created. Secondly, the pore size distribution curves for the precipitated materials reveal several features. Fig. 1 shows the pore size distribution curve for pure gallium oxide prepared via a precipitation route. The pores are mostly of less than 100 angstroms in diameter and the distribution is very narrow. Similarly, Fig. 2

10 illustrates that the pore distribution of a pure aluminium oxide material formed by precipitation is also characterized by pores of dimension less than 100 angstroms. Examination of the pore size distribution plots for 10% and 20% gallium aluminium oxide samples [Fig. 3 & 4] reveals that the small pore size diameter is maintained and moreover, on average smaller pores are present in the mixed gallium aluminium oxide

15 samples relative to pure gallium oxide or pure aluminium oxide. Again, an essentially unimodal distribution of pore sizes is evident which may indicate formation of a true mixed gallium aluminium oxide phase.

Further evidence for the formation of a mixed gallium aluminium oxide phase is gained from inspection of XRD traces [Fig. 5]. The profile recorded for both 10 and

20 20wt% gallium aluminium oxide materials is very similar to that observed for pure alumina. This information may indicate the formation of solid solutions of gallium in aluminium oxide as proposed by Foster and Stumpf (J. Am. Chem. Soc., 73, 1590, (1951)).

The apparatus of the twenty first embodiment of this invention typically comprises

25 an inlet for the introduction of  $\text{NO}_x$  containing gases, a housing which comprises the catalyst systems of this invention and an outlet for the expiration of the gases once the  $\text{NO}_x$  is reduced by the catalyst systems of this invention. Still typically, the apparatus includes catalytic units used in the exhaust systems of automotive vehicles and those units which are utilised in the treatment of exhaust gases for industrial stacks. Still more

30 typically, catalytic monoliths which comprise catalyst systems coated on the inner face of the housing and which are used in automotive exhaust systems are included within the apparatus of this invention. These apparatus may further comprise filters, suitable supports, stabilisers, and other catalytic materials.

The gallium aluminium oxide material may be further enhanced in catalytic activity

35 by addition of any element or combination of elements already known to those skilled in

the art which have been previously applied to alumina based catalysts for NO<sub>x</sub> removal. Addition of such elements may be achieved by any known means and is not particularly limited. However, commonly the additives may be deposited on the oxide carrier by means of impregnation with a soluble salt followed by drying to remove excess water and calcination at elevated temperature to convert the additive to the oxidic phase.

Also, further known characteristics and features of catalyst systems, supports, physical characteristics, etc which are described in *Wijngaarden, Kronberg & Westerterp "Industrial Catalysis – Optimizing Catalysts and Processes" published 1998 Wiley-VCH Verlag GmbH* are included within the scope of this invention.

### Brief Description of the Drawings

The invention will now be described, by way of example only, with reference to the accompanying figures; in which:

Fig. 1 depicts a BJH pore size distribution curve for pure gallium oxide prepared via a precipitation route;

Fig. 2 depicts a BJH pore size distribution curve for pure aluminium oxide prepared via a precipitation route;

Fig. 3 depicts a BJH pore size distribution curve for 10% gallium aluminium oxide prepared via a precipitation route;

Fig. 4 depicts a BJH pore size distribution curve for 20% gallium aluminium oxide prepared via a precipitation route;

Fig. 5 depicts XRD patterns for gallium oxide, aluminium oxide and 10 & 20wt% gallium aluminium oxide samples;

Fig. 6 depicts the effect of the amount of gallium incorporation into the structure of alumina with regard to selective catalytic reduction of NO with propene;

Fig. 7 depicts the effect of the amount of gallium incorporated in the structure of aluminium oxide upon the catalytic activity for selective catalytic reduction of NO by propene;

Fig. 8 depicts the effect of GHSV upon the NO reduction performance of a 10wt% gallium aluminium oxide catalyst;

Fig. 9 depicts the promoting effect of indium upon the activity of a 10wt% gallium aluminium oxide catalyst;

Fig. 10 depicts the effect of water in the gas stream upon the performance of a 20wt% gallium aluminium oxide catalyst and the promoting effect of 0.1% tungsten addition to the latter catalyst;

Fig. 11 depicts the activity of a 1wt% tungsten/20wt% gallium aluminium oxide catalyst for SCR of NO with propene in the presence of water and the effect of propene concentration;

Fig. 12 depicts the activity of a 2wt% silver/20wt% gallium aluminium oxide catalyst for SCR of NO with propene in the presence of water;

Fig. 13 depicts the activity of 0.1 and 2wt% tin/20wt% gallium aluminium oxide catalysts for SCR of NO with propene in the presence of water;

Fig. 14 depicts the activity of a 20wt% gallium aluminium oxide catalyst for SCR of NO with methane in the presence of water;

Fig. 15 depicts the activity of a Co-ZSM-5 catalyst for SCR of NO with methane in the presence of water;

Fig. 16 depicts the activity of a 2% Ag/20wt% gallium aluminium oxide catalyst for SCR of NO with methane in the presence of water;

Fig. 17 depicts the activity of a 1% Ir/20wt% gallium aluminium oxide catalyst for SCR of NO with methane in the presence of water;

Fig. 18 depicts the activity of a 0.1% Pd/20wt% gallium aluminium oxide catalyst for SCR of NO with methane in the presence of water;

Fig. 19 depicts the activity of a 2% Ag/2% W/20wt% gallium aluminium oxide catalyst for SCR of NO with methane in the presence of water; and

Fig. 20 depicts the activity of a 0.1% Rh/20wt% gallium aluminium oxide catalyst for SCR of NO with methane in the presence of water

### Examples

Detailed descriptions of the preferred embodiment are provided herein. It is to be understood, however, that the present invention may be embodied in various forms. Therefore, specific details disclosed herein are not to be interpreted as limiting the generality of the above description.

#### Example 1

0.1894g  $\text{Ga}(\text{NO}_3)_3$  hydrate was dissolved in 20mL  $\text{H}_2\text{O}$  and 25g of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  was dissolved in 40mL  $\text{H}_2\text{O}$ . A solution of pH 8 was prepared using  $\text{NH}_4\text{OH}$  as buffer, and a total volume of 50mL was prepared. The  $\text{Ga}(\text{NO}_3)_3$  solution and  $\text{Al}(\text{NO}_3)_3$  solution were added together, and the resultant solution was characterized by a  $\text{pH} < 1$ . This combined solution was then added in 5mL portions to the pH 8 solution of ammonium hydroxide, and the pH readjusted to pH 8 using  $\text{NH}_4\text{OH}$  solution. The final pH of the solution was 8.01. The precipitate was collected by means of vacuum filtration and then dried in a 450W microwave for 15 minutes. Finally, the catalyst was calcined at  $500^\circ\text{C}$

for 4 hours. The weight of the calcined sample was 3.11g and it contained 1% on a weight basis of nominally gallium oxide ( $\text{Ga}_2\text{O}_3$ ).

The activity of the 1% gallium aluminium oxide catalyst was evaluated using a gas mixture consisting of;

$$\text{NO} = 500 \text{ ppm}$$

$$\text{C}_3\text{H}_6 = 700 \text{ ppm}$$

$$\text{O}_2 = 9\%$$

$$\text{CO} = 1500 \text{ ppm}$$

$$\text{CO}_2 = 12\%$$

and a total flow rate such that the GHSV =  $100,000 \text{ h}^{-1}$ . The extent of NO conversion to nitrogen as a function of catalyst temperature is shown in Fig. 6.

### Example 2

3.788g  $\text{Ga}(\text{NO}_3)_3$  hydrate was dissolved in 20mL  $\text{H}_2\text{O}$  and 50g of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  was dissolved in 70mL  $\text{H}_2\text{O}$ . A solution of pH 8 was prepared using  $\text{NH}_4\text{OH}$  as buffer, and a total volume of 100mL was prepared. The  $\text{Ga}(\text{NO}_3)_3$  solution and  $\text{Al}(\text{NO}_3)_3$  solution were added together, and the resultant solution was characterized by a  $\text{pH} < 1$ . This combined solution was then added in 5mL portions to the pH 8 solution of ammonium hydroxide, and the pH readjusted to pH 8 using  $\text{NH}_4\text{OH}$  solution. The final pH of the solution was 8.01. The precipitate was collected by means of vacuum filtration and then dried in a 450W microwave for 15 minutes. Finally, the catalyst was calcined at  $500^\circ\text{C}$  for 4 hours. The weight of the calcined sample was 7.1g and it contained 10% on a weight basis of nominally gallium oxide ( $\text{Ga}_2\text{O}_3$ ).

Catalytic testing for deNOx activity was performed in the same manner as outlined for example 1 [Fig. 6].

### Example 3

3.788g  $\text{Ga}(\text{NO}_3)_3$  hydrate was dissolved in 20 mL  $\text{H}_2\text{O}$  and 25g of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  was dissolved in 40mL  $\text{H}_2\text{O}$ . A solution of pH 8 was prepared using  $\text{NH}_4\text{OH}$  as buffer, and a total volume of 50mL was prepared. The  $\text{Ga}(\text{NO}_3)_3$  solution and  $\text{Al}(\text{NO}_3)_3$  solution were added together, and the resultant solution was characterized by a pH of *Ca.* 1. This combined solution was then added in 5mL portions to the pH 8 solution of ammonium

hydroxide, and the pH readjusted to pH 8 using  $\text{NH}_4\text{OH}$  solution. The final pH of the solution was 7.98. The precipitate was collected by means of vacuum filtration and then dried in a 450W microwave for 15 minutes. Finally, the catalyst was calcined at  $500^\circ\text{C}$  for 4 hours. The weight of the calcined sample was 4.0lg and it contained 20% on a weight basis of nominally gallium oxide ( $\text{Ga}_2\text{O}_3$ ).

Catalytic testing for deNOx activity was performed in the same manner as outlined for example 1 [Fig. 6].

For clarity the maximum NO conversion to nitrogen as a function of gallium incorporation into the aluminium oxide structure is displayed in Fig. 7. It is apparent that the activity increases dramatically upon only small amounts of gallium addition and does not increase as markedly as the gallium loading is further increased. Hence, in practical terms a loading of 20wt% may be commercially attractive although there is no technical limit to increasing this loading of gallium further.

#### Comparative Example 1

A precipitated gallium oxide sample was prepared as follows. 5.114g  $\text{Ga}(\text{NO}_3)_3$  hydrate was dissolved in 20mL  $\text{H}_2\text{O}$  and subsequently, a solution of aqueous ammonia was added dropwise to induce precipitation of gallium hydroxide. The final pH was approximately pH = 9. The precipitate was collected by vacuum filtration and further dried in a 450W microwave oven for 15 min. The sample was calcined at  $120^\circ\text{C}$  for four hours and then at  $550^\circ\text{C}$  for four hours. The weight of the gallium oxide sample thus prepared was 0.99g.

Catalytic testing for deNOx activity was performed in the same manner as outlined for example 1. Notably, the activity of pure gallium oxide was surprisingly less than the efficiency of mixed gallium aluminium oxide materials [Fig. 6].

#### Comparative Example 2

A precipitated aluminium oxide sample was prepared as follows according to a precipitation method described by Saha *et al.* (S.K. Saha and P. Pramanik, *Journal of Materials Science* **29**, 3425-3429 (1994)). Aluminium hydroxide was completely precipitated from a solution of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (37.5g/100mL) by adding ammonium hydroxide (approx 22mL). The resulting slurry was then filtered, washed with  $\text{H}_2\text{O}$  (100mL), and oven dried at  $100^\circ\text{C}$  overnight. The sample was then calcined at  $550^\circ\text{C}$  for 2 hours.

Catalytic testing for deNOx activity was performed in the same manner as outlined for example 1. Significantly, the activity of pure precipitated alumina for NOx removal

was substantially less than that observed for mixed gallium aluminium oxide materials [Fig.6].

#### Example 4

Fig. 8 illustrates the performance of a 10wt% gallium aluminium oxide catalyst for NO removal (using the conditions employed in example 1) as a function of space velocity. Importantly, even at exceptionally high values of GHSV, *e.g.* 200,000 h<sup>-1</sup>, the rate of NO removal is still in excess of 70%.

#### Example 5

0.1% indium was impregnated on a 10wt% gallium aluminium oxide sample by means of dissolving an appropriate amount of indium chloride in water and adding this solution to a sample of 10wt% gallium aluminium oxide. Subsequently, the catalyst was dried at 120°C and then calcined in air at 550°C for 2 h. The catalytic activity for NO reduction was evaluated using the same test conditions as those outlined in example 1. Notably, Fig. 9 shows that the performance of the gallium aluminium oxide support can be improved by the addition of elements known to those skilled in the art, such as indium.

#### Example 6

It is important to prepare catalysts which display NO<sub>x</sub> reduction capacity even in the presence of significant percentages of water (as commonly encountered in commercial situations). Fig. 10 shows the performance of 20wt% gallium aluminium oxide in a gas mixture comprising of;

$$\text{NO} = 500 \text{ ppm}$$

$$\text{C}_3\text{H}_6 = 700 \text{ ppm}$$

$$\text{O}_2 = 9\%$$

$$\text{CO} = 1500 \text{ ppm}$$

$$\text{CO}_2 = 12\%$$

$$\text{H}_2\text{O} = 7.5\%$$

and at a flow rate which resulted in a GHSV of 100,000 h<sup>-1</sup>.

Although, the overall NO reduction activity was diminished in comparison to the case where water was absent, the removal of NO was still in excess of 50% at temperatures exceeding 600°C.

#### Example 7

5 A 0.1%  $\text{WO}_3$  on 20wt% gallium aluminium oxide catalyst was prepared as follows. 0.999g of 20wt% gallium aluminium oxide was added to a solution of 0.0011g  $(\text{NH}_4)_6\text{W}_{12}\text{O}_{39} \cdot x\text{H}_2\text{O}$  dissolved in 2mL  $\text{H}_2\text{O}$ . The resulting slurry was dried at 120°C, then calcined in air at 550°C for four hours. The catalyst was then evaluated for NO reduction activity using the gas mixture and space velocity described in example 6. Fig. 10 shows that the presence of 0.1wt% tungsten improved the catalytic performance of the gallium aluminium oxide catalyst.

#### Example 8

A 1%  $\text{WO}_3$  on 20wt% gallium aluminium oxide catalyst was prepared in a similar manner to the catalyst described in example 7 with the only difference being that the amount of tungsten precursor used was suitably increased. The catalyst was then evaluated for NO reduction activity using the gas mixture and space velocity described in example 6. Fig. 11 shows that the catalytic activity for NO removal was exceptionally high for this system. Indeed, when a larger concentration of propylene was present (1000 ppm) the conversion of NO to nitrogen was in excess of 90%.

#### Example 9

A 2wt% silver on 20wt% gallium aluminium oxide catalyst was prepared as follows. An appropriate amount of silver nitrate was dissolved in a solution of dilute HCl. This solution was then added to 0.99 g of 20wt% gallium aluminium oxide to form a slurry. This material was then dried at 120°C and then calcined at 550°C for four hours. Catalytic testing was performed in the same manner as described in example 6. Fig. 12 shows that the presence of silver on the gallium aluminium oxide material not only promotes catalyst activity in the presence of water but also exhibits activity at a lower temperature range (relative to the previous use of tungsten on gallium aluminium oxide).

#### Example 10

0.999 g of 20% gallium-alumina was added to a solution of 0.0022 g  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  dissolved in 3mL of 2:1 aqueous HCl. The slurry was dried at 120°C, then calcined in air at 550°C for four hours. The weight of the calcined sample was 0.76g and it comprised of 0.1% by weight of tin. Catalytic testing was performed in the same manner as described in example 6. Fig. 13 shows that the addition of tin to a gallium aluminium



oxide catalyst further increases the NO conversion with conversions determined to be in excess of 70% at 600°C.

### Example 11

A 2wt% tin on 20wt% gallium aluminium oxide catalyst was prepared in an analogous manner to the catalyst described in example 10, the only difference being that the amount of tin precursor used was appropriately increased. Catalytic testing was performed in the same manner as described in example 6. The employment of a higher tin loading resulted in the maximum NO reduction activity decreasing, however, the NO conversion at lower temperatures (less than or equal to 550°C) was increased [Fig. 13]. Therefore, this example demonstrates how the catalysts of this invention can be modified to exhibit NO reduction activity at various temperatures of choice.

### Example 12

A 20wt% gallium aluminium oxide catalyst was evaluated for NO removal activity using methane as the hydrocarbon reductant. The following test conditions were used;

$$\text{NO} = 500 \text{ ppm}$$

$$\text{CH}_4 = 2000 \text{ ppm}$$

$$\text{O}_2 = 9\%$$

$$\text{CO} = 1500 \text{ ppm}$$

$$\text{CO}_2 = 12\%$$

$$\text{H}_2\text{O} = 7.5\%$$

and the flow rate employed was sufficient to give a GHSV of 100,000 h<sup>-1</sup>. Fig. 14 shows that the gallium aluminium oxide catalyst was active for the selective catalytic reduction of NO with methane.

### Comparative Example 3

A precipitated alumina sample was evaluated for the selective catalytic reduction of NO with methane according to the test conditions described in example 12. The conversion of NO to nitrogen was found to be zero over the temperature studied (200-650°C).

**Comparative Example 4**

A cobalt exchanged zeolite was prepared by conventional ion-exchange procedures. Briefly, a solution of cobalt acetate was refluxed with Na-ZSM-5 (Uetikon,  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 25$ ) and then dried at 120°C for several hours and then calcined at 500°C in air for 2 hours. The activity of this catalyst for selective catalytic reduction of NO with methane was measured using the test conditions described in example 12. Notably, the conversion of NO to nitrogen was never in excess of 25% [Fig. 15] and moreover, the thermal stability of zeolite samples is well known to those skilled in the art to be unsuitable for commercial application.

**Example 13**

A 2wt% silver on 20wt% gallium aluminium oxide catalyst was prepared as follows. An appropriate amount of silver nitrate was dissolved in a solution of dilute HCl. This solution was then added to 0.99 g of 20wt% gallium aluminium oxide to form a slurry. This material was then dried at 120°C and then calcined at 550°C for four hours. The activity of this catalyst for selective catalytic reduction of NO with methane was measured using the test conditions described in example 12. Notably, the presence of silver further enhanced the activity of the catalyst for SCR of NO with methane relative [Fig. 16] to the case with the gallium-alumina material alone.

**Example 14**

A 1wt% iridium on 20wt% gallium aluminium oxide catalyst was prepared as follows. An appropriate amount of iridium chloride was dissolved in water and this solution was then added to an appropriate amount of 20wt% gallium aluminium oxide to form a slurry. This material was then dried at 120°C and then calcined at 550°C for four hours. The activity of this catalyst for selective catalytic reduction of NO with methane was measured using the test conditions described in example 12. This catalyst was again active for the SCR of NO with methane [Fig. 17].

**Example 15**

A 0.1wt% palladium on 20wt% gallium aluminium oxide catalyst was prepared as follows. An appropriate amount of palladium tetra-ammine chloride was dissolved in water and this solution was then added to an appropriate amount of 20wt% gallium aluminium oxide to form a slurry. This material was then dried at 120°C and then calcined at 550°C for four hours. The activity of this catalyst for selective catalytic reduction of NO with methane was measured using the test conditions described in example 12. This catalyst was again active for the SCR of NO with methane [Fig. 18].

**Example 16**

A 2wt% silver/2wt% tungsten on 20wt% gallium aluminium oxide catalyst was prepared as follows. An appropriate amount of silver nitrate and ammonium metatungstate was dissolved in water and this solution was then added to an appropriate amount of 20wt% gallium aluminium oxide to form a slurry. This material was then dried at 120°C and then calcined at 550°C for four hours. The activity of this catalyst for selective catalytic reduction of NO with methane was measured using the test conditions described in example 12. This catalyst was again active for the SCR of NO with methane [Fig. 19].

**Example 17**

A 0.1wt% rhodium on 20wt% gallium aluminium oxide catalyst was prepared as follows. An appropriate amount of rhodium chloride was dissolved in water and this solution was then added to an appropriate amount of 20wt% gallium aluminium oxide to form a slurry. This material was then dried at 120°C and then calcined at 550°C for four hours. The activity of this catalyst for selective catalytic reduction of NO with methane was measured using the test conditions described in example 12. This catalyst was very active for the selective catalytic reduction of NO with methane with the maximum conversion noted to be in excess of 50% [Fig. 20].

**Table 1 : Surface areas of alumina and gallium oxide compared with various co-precipitated gallium-alumina samples**

Catalyst	Surface Area (m <sup>2</sup> /g)
alumina	197
gallium oxide	88
1 % Ga-alumina	201
5 % Ga-alumina	227
10 % Ga-alumina	233
15 % Ga-alumina	234
20 % Ga - alumina	225

The aforementioned examples serve to illustrate the advantages of the catalysts, catalytic systems, where the combination of the aluminium oxide and the oxide of a metal, different to aluminium oxide particularly gallium oxide provides a synergistic effect when compared to aluminium oxide and gallium oxide alone. The catalyst system particularly provides advantages in the selective reduction of NO<sub>x</sub> when using reductants such as hydrocarbons, aldehydes and alcohols particularly methane and propene, reduction of NO<sub>x</sub> present in lean burn engine exhausts, reduction of NO<sub>x</sub> emitted from diesel engines, reduction of NO<sub>x</sub> from stationary combustion sources, reduction of NO<sub>x</sub> from natural gas fuelled vehicles, resistance to thermal degradation, resistance to deactivation by water at elevated temperatures and resistance to poisoning by oxides of sulfur.

Those skilled in the art will appreciate that the scope of this invention includes all modifications and variations such as would be apparent to a skilled person, and that the scope of this invention is not to be restricted to the specific examples and embodiments described above. This invention further includes all steps, processes, intermediates and applications therefore.

Throughout this specification, unless the context clearly indicates otherwise, the words "comprise", "comprises", "comprising", and variations thereof shall be understood as meaning that the stated integer is inclusive of other integers even though those other integers are not explicitly stated.

## CLAIMS:

1. A catalyst system for reduction of oxides of nitrogen comprising:
  - a) aluminium oxide; and
  - b) at least one metal oxide which is different to aluminium oxide.
- 5 2. The catalyst system of claim 1 wherein said at least one metal oxide is selected from the group consisting of boron oxide, gallium oxide and a mixture of boron oxide and gallium oxide.
3. The catalyst system of claim 1 wherein said catalyst system further comprises:
  - c) a promoting agent.
- 10 4. The catalyst system of claim 3 wherein said promoting agent comprises:
  - c) a promoting agent selected from the group of a noble metal, alkaline earth metal, rare earth element, an element of group 4A in the periodic table, an element of group 5A in the periodic table.
5. The catalyst system of claim 2 wherein said catalyst system comprises:
  - 15 b) gallium oxide; and
  - c) a promoting agent.
6. The catalyst system of claim 5 wherein said promoting agent comprises:
  - c) a promoting agent selected from the group of a noble metal, alkaline earth metal, rare earth element, an element of group 4A in the periodic table, an element of group 5A in the periodic table.
- 20 7. The catalyst system of claim 2 wherein said catalyst system comprises:
  - b) a mixture of gallium oxide and boron oxide; and
  - c) a promoting agent.
8. The catalyst system of claim 7 wherein said promoting agent comprises:
  - 25 c) a promoting agent selected from the group of a noble metal, alkaline earth metal, rare earth element, an element of group 4A in the periodic table, an element of group 5A in the periodic table.
9. The catalyst system of claim 2 wherein said catalyst system comprises:
  - b) boron oxide; and
  - 30 c) a promoting agent.
10. The catalyst system of claim 9 wherein said promoting agent comprises:
  - c) a promoting agent selected from the group of a noble metal, alkaline earth metal, rare earth element, an element of group 4A in the periodic table, an element of group 5A in the periodic table.
- 35 11. The catalyst system of claim 2 wherein said catalyst system comprises:

- b) 1 to 50 wt% of at least one metal oxide.
12. The catalyst system of claim 2 wherein said catalyst system comprises:
- b) 1 to 50 wt% gallium oxide.
13. The catalyst system of claim 5 wherein said catalyst system comprises:
- 5 b) 1 to 50 wt% gallium oxide.
14. The catalyst system of claim 8 wherein said catalyst system comprises:
- b) 1 to 50 wt% gallium oxide.
15. The catalyst system of claim 2 wherein said catalyst system comprises:
- b) 1 to 25 wt% gallium oxide.
- 10 16. The catalyst system of claim 5 wherein said catalyst system comprises:
- b) 1 to 25 wt% gallium oxide.
17. The catalyst system of claim 6 wherein said catalyst system comprises:
- b) 1 to 25 wt% gallium oxide.
18. The catalyst system of claim 8 wherein said catalyst system comprises:
- 15 b) 1 to 50 wt% gallium oxide.
19. An automotive exhaust catalyst system for reducing oxides of nitrogen comprising a a automotive exhaust catalyst support together with the catalyst system of any one of claims 1 to 18.
20. A catalyst system for reducing oxides of nitrogen from combustion sources
- 20 comprising a catalyst support together with the catalyst system of any one of claims 1 to 18.
21. A method of preparing a catalyst system comprising:
- a) mixing a precursor of aluminium oxide and a precursor of a metal oxide which is different to aluminium oxide;
- 25 b) adding a basic compound;
- c) drying and heating the resulting mixture;
- so as to form a catalytic system for reduction of oxides of nitrogen.
22. The method of claim 21 wherein step a) comprises:
- a) mixing a precursor of aluminium oxide and a precursor of at least one
- 30 metal oxide is selected from the group consisting of boron oxide, gallium oxide and a mixture of boron oxide and gallium oxide.
23. A method of preparing an automotive catalyst system comprising:
- a) mixing a precursor of aluminium oxide and a precursor selected from the
- group consisting of a precursor of boron oxide, gallium oxide and a mixture of boron
- 35 oxide and gallium oxide;

- b) adding a basic compound;
- c) drying and heating the resulting mixture;
- d) forming a catalytic system for reduction of oxides of nitrogen; and
- e) impregnating said catalytic system on a support material.

5        24. A process for removing oxides of nitrogen from exhaust gas from a combustion source comprising:

- a) impregnating a catalyst support with aluminium oxide and at least one metal oxide is selected from the group consisting of boron oxide, gallium oxide and a mixture of boron oxide and gallium oxide;
- 10        b) directing a reductant and exhaust gas containing oxides of nitrogen over the impregnated catalyst support whereby the oxides of nitrogen in said gas are reduced.

25. The process of claim 23 or 24 wherein the reductant is selected from the group of a hydrocarbon, hydrogen, an aldehyde and an alcohol.

15        26. A process for removing oxides of nitrogen from exhaust gas from a combustion source comprising:

directing a reductant and exhaust gas containing oxides of nitrogen over the a catalyst system of any one of claims 1, 11 to 17 whereby the oxides of nitrogen in said gas are reduced.

20        27. A process for removing oxides of nitrogen from exhaust gas from a combustion source comprising:

directing a reductant and exhaust gas containing oxides of nitrogen over the a catalyst support impregnated with a catalyst system of any one of claims 1, 11 to 17 whereby the oxides of nitrogen in said gas are reduced.

28. The catalyst system of claim 6 wherein said catalyst system comprises:

- 25        b) 1 to 50 wt% gallium oxide.

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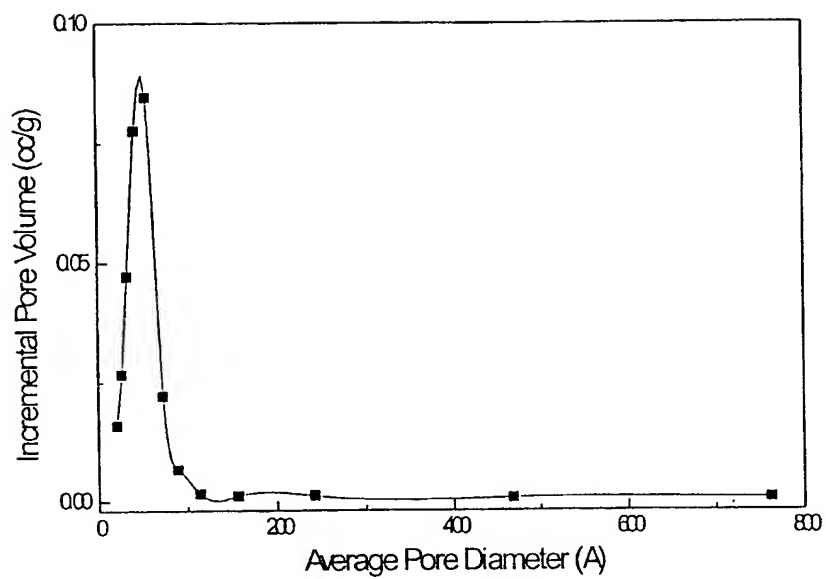


Fig. 1

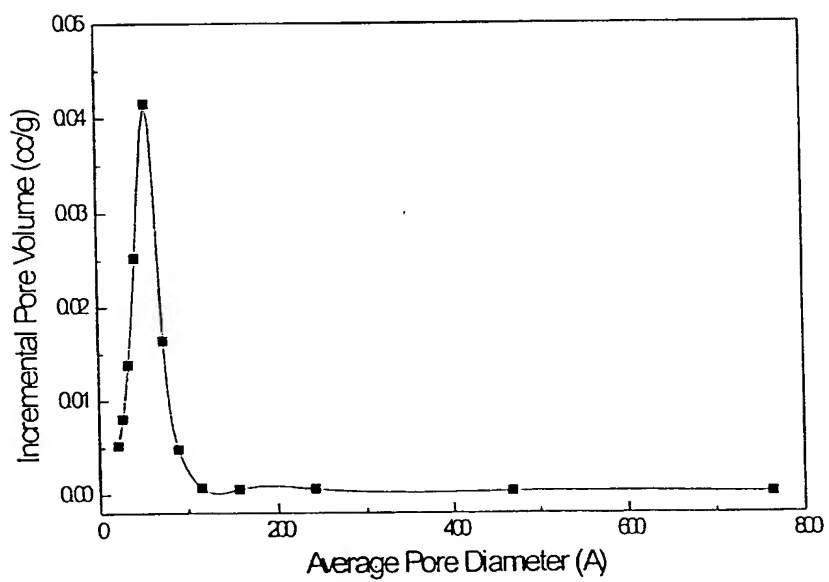


Fig. 2



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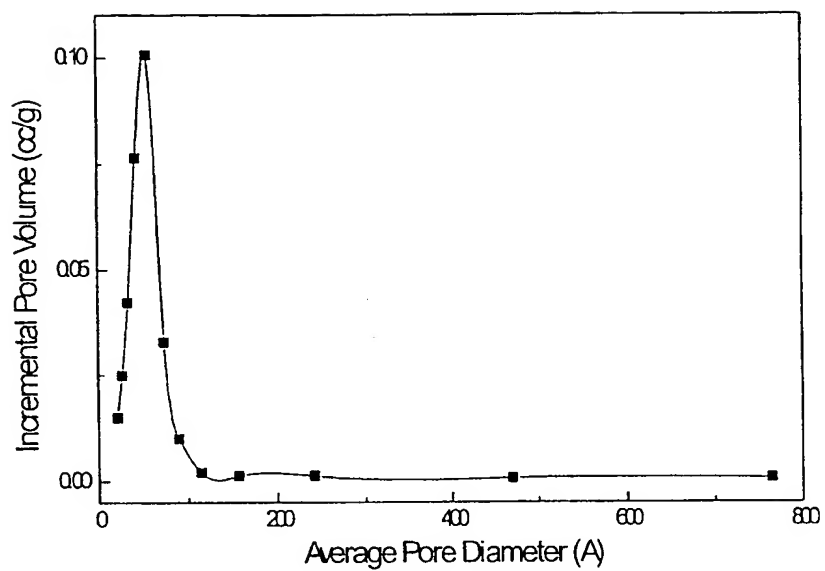


Fig. 3

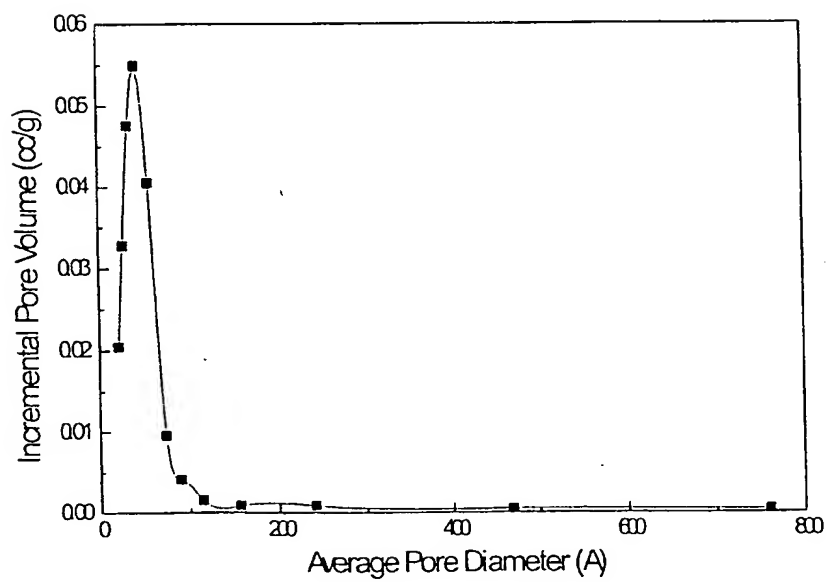


Fig. 4

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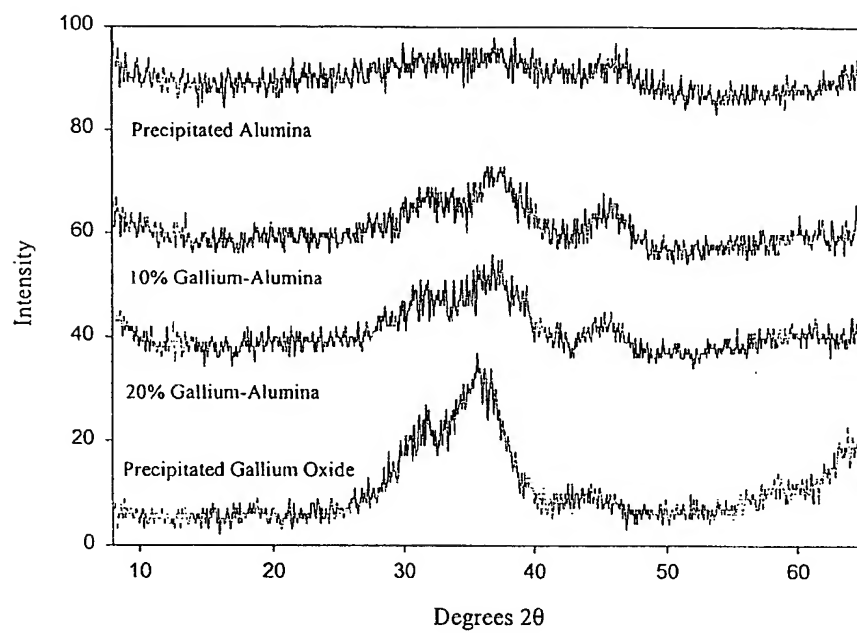


Fig. 5

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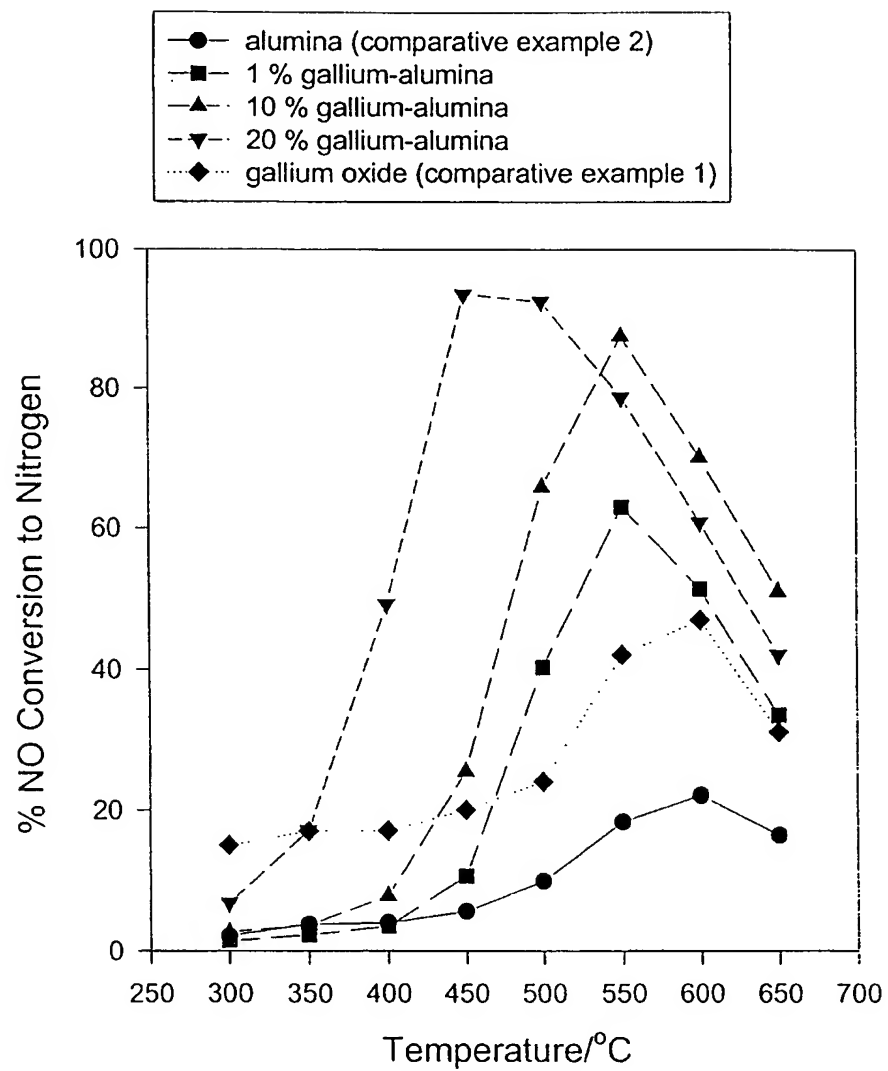


Fig. 6

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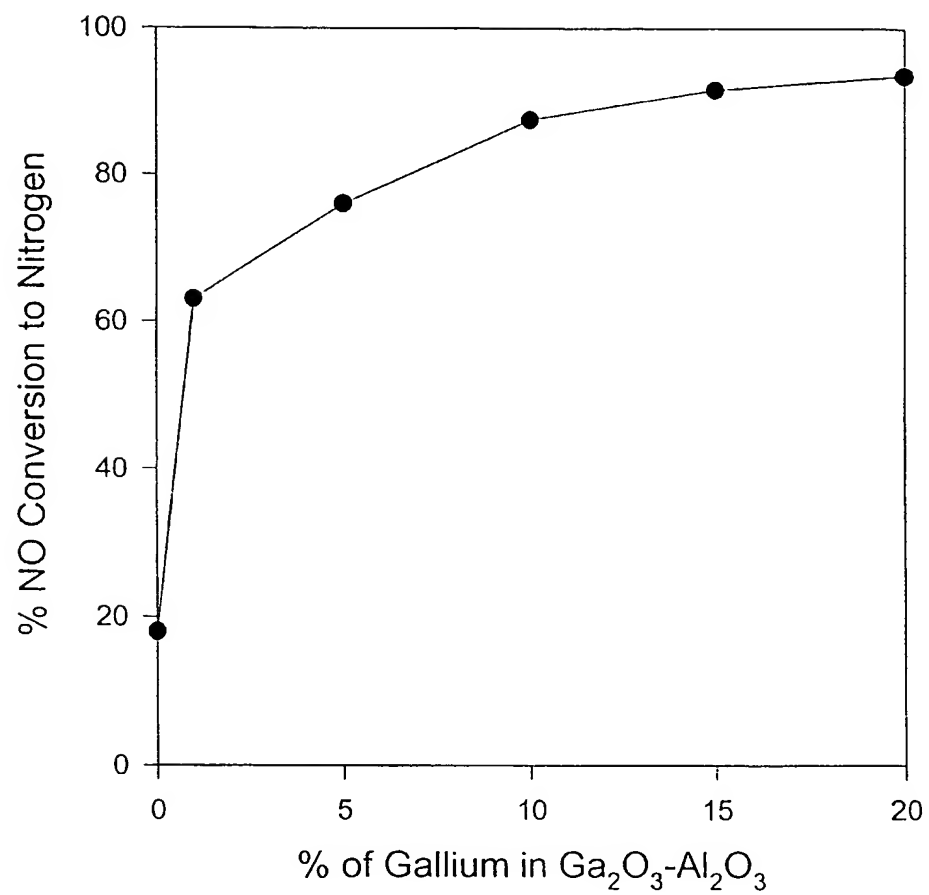


Fig. 7 ;

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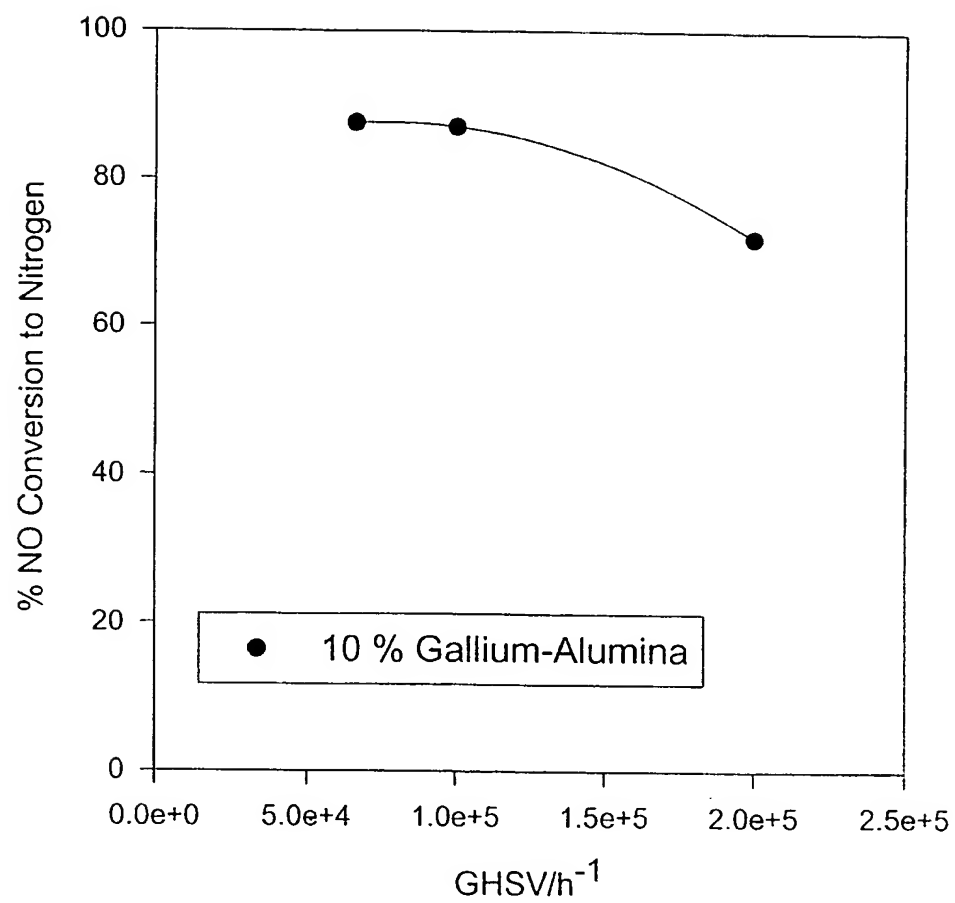


Fig. 8 ;

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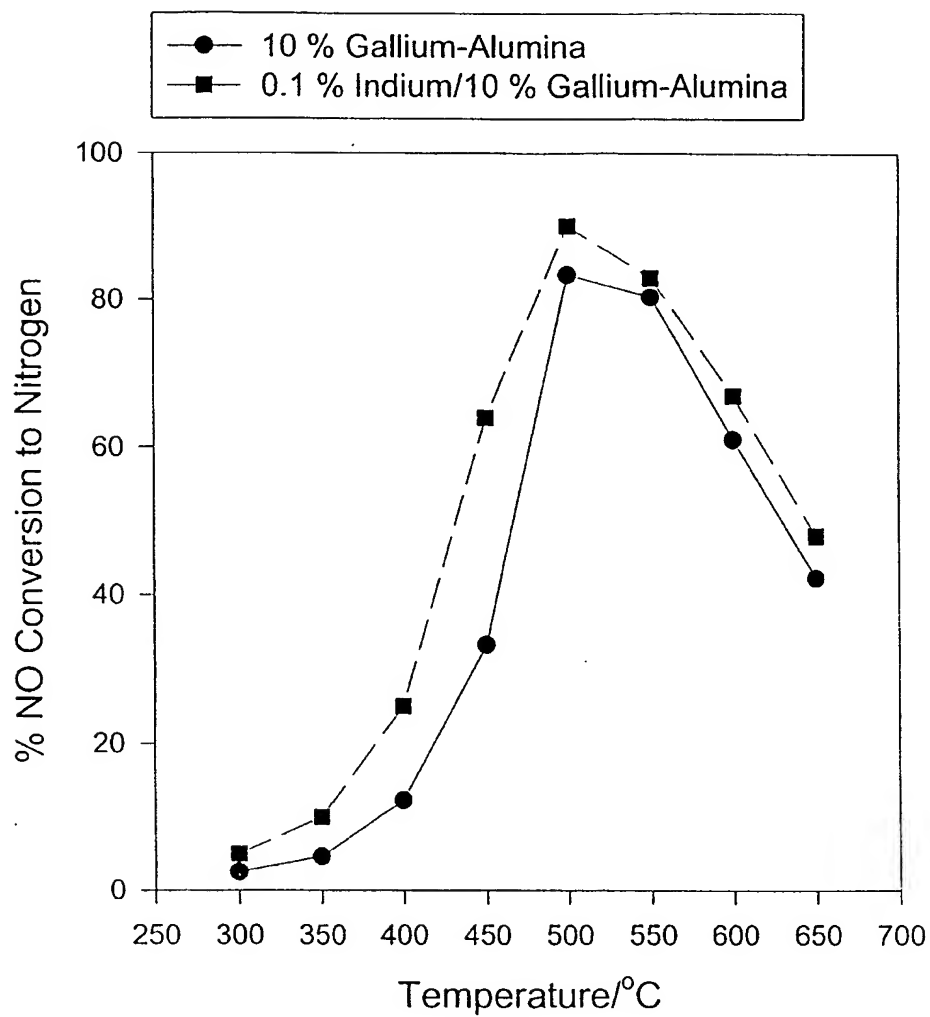


Fig. 9 ;

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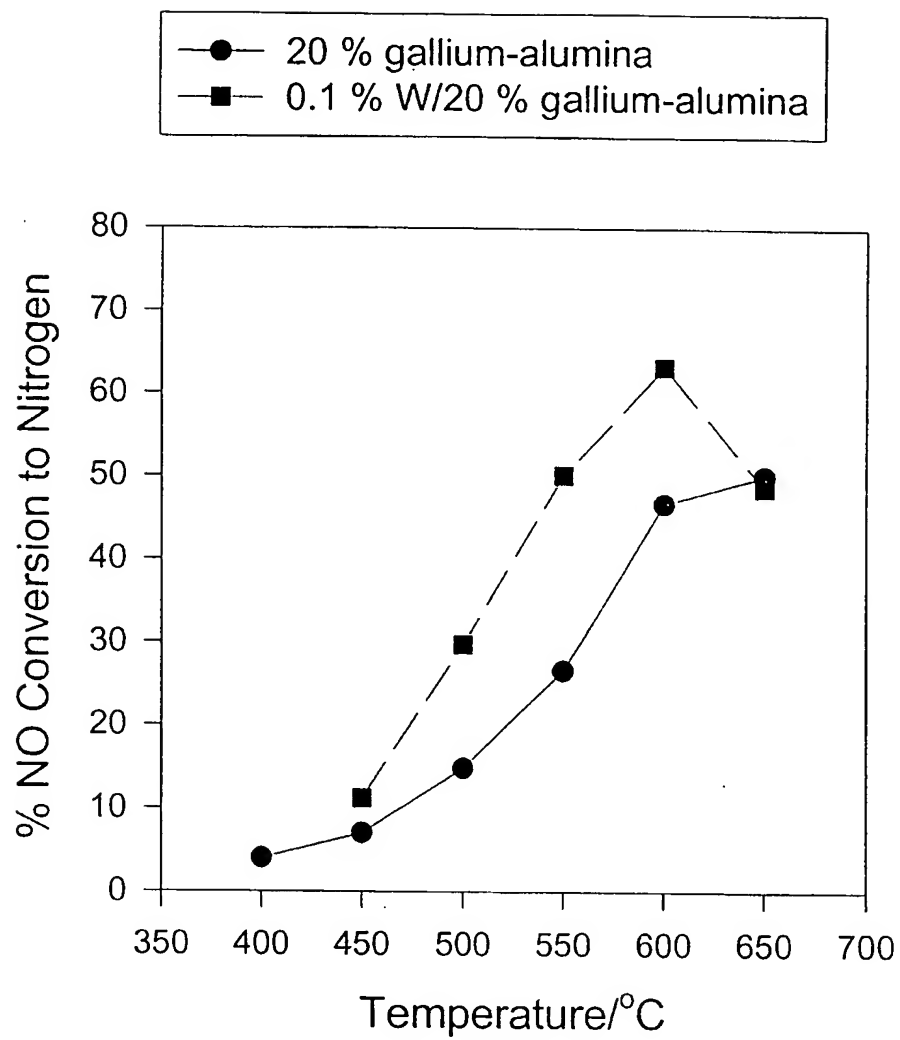


Fig. 10

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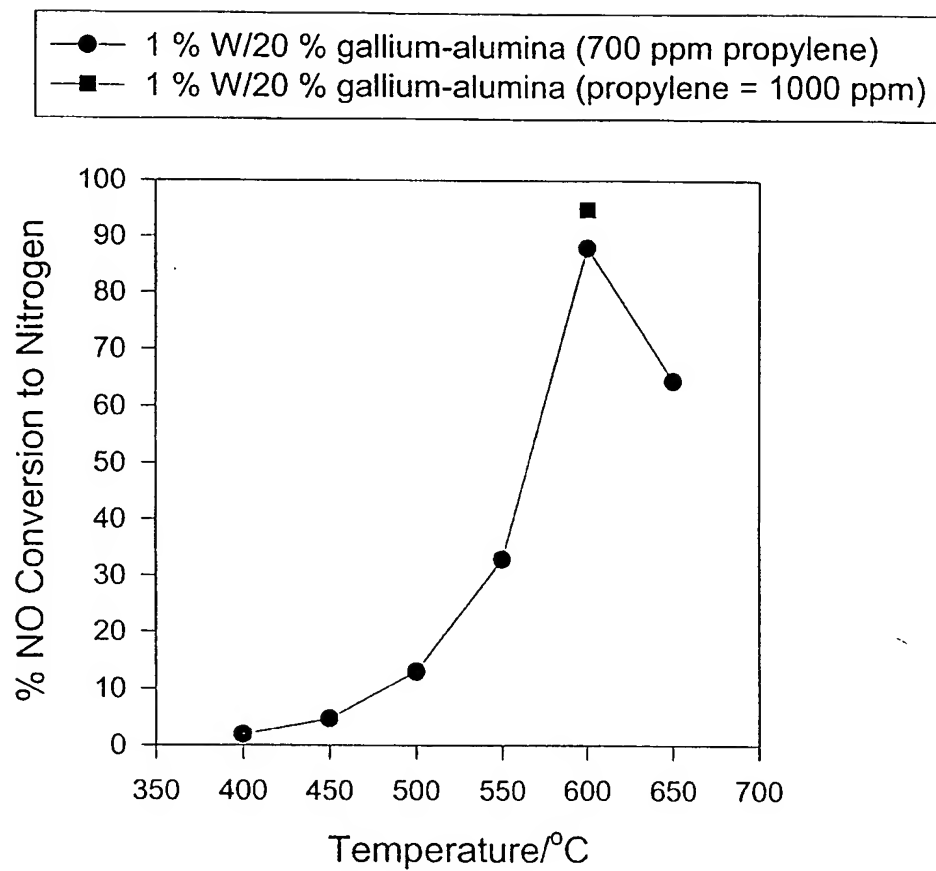


Fig. 11



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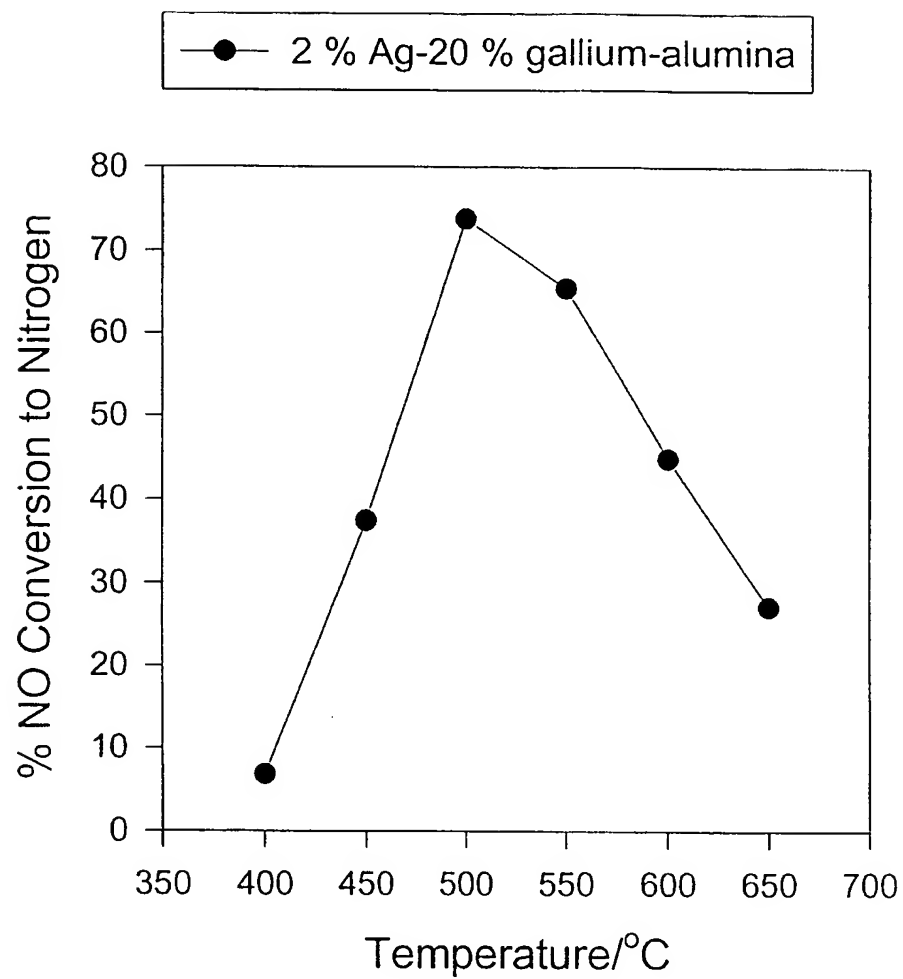


Fig. 12

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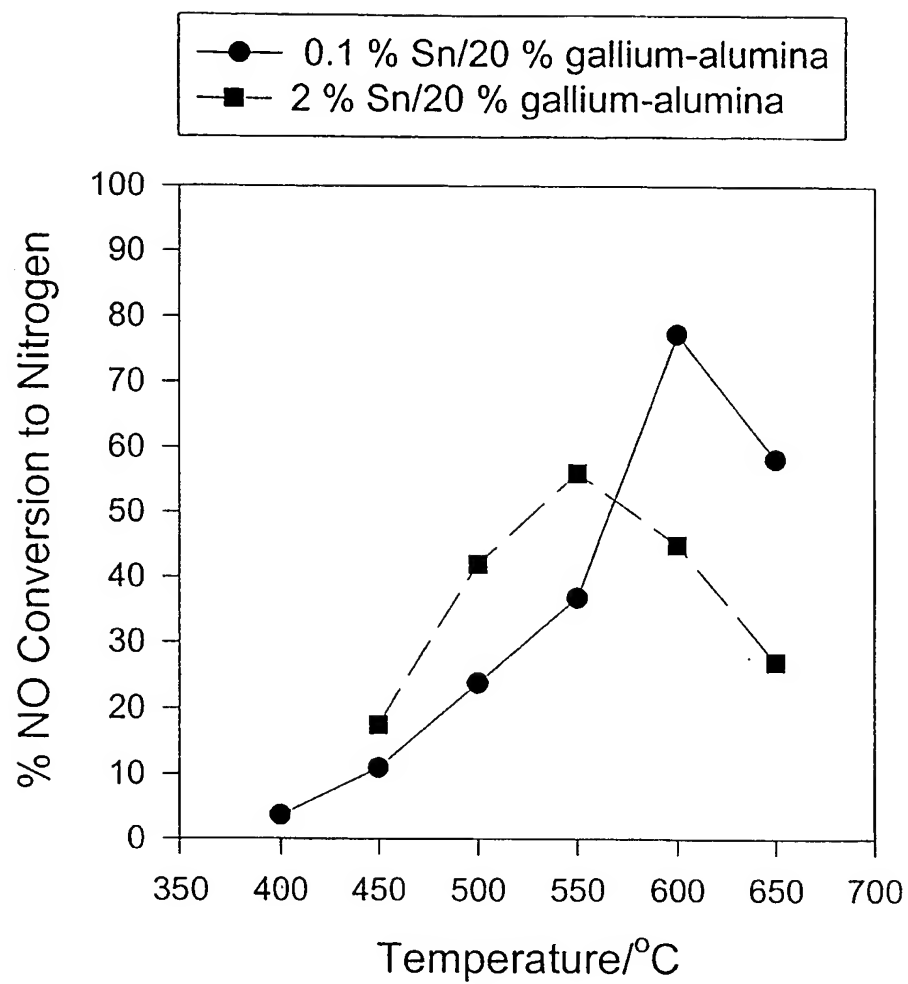


Fig. 13

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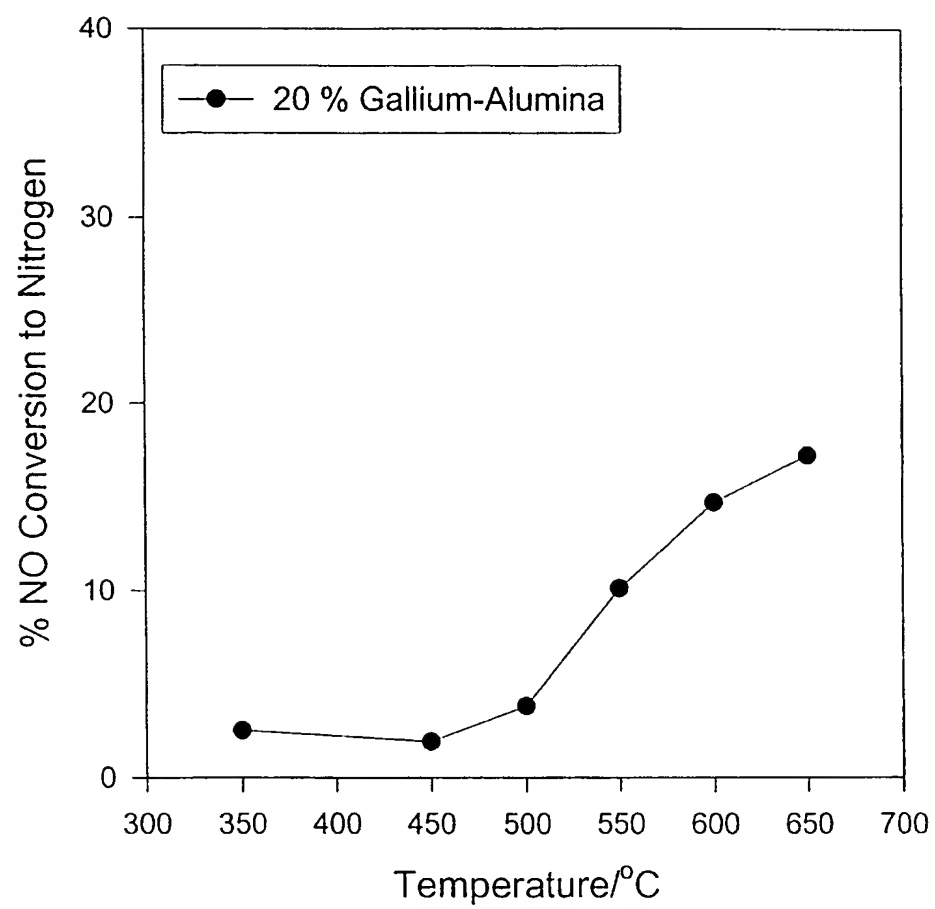


Fig. 14

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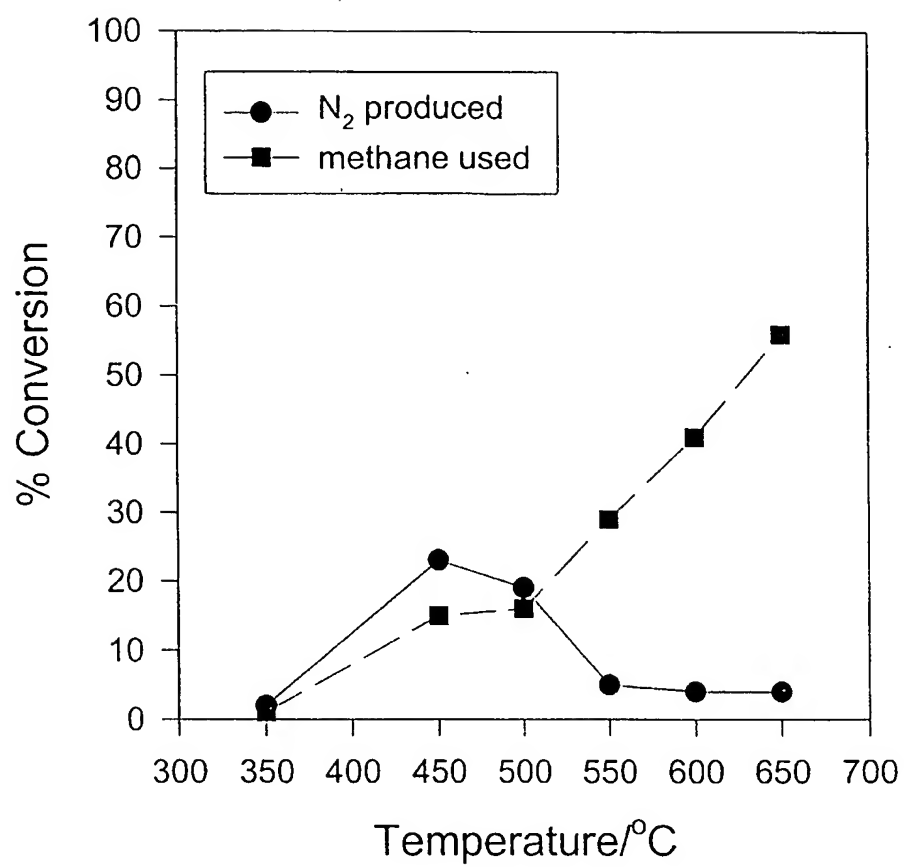


Fig. 15

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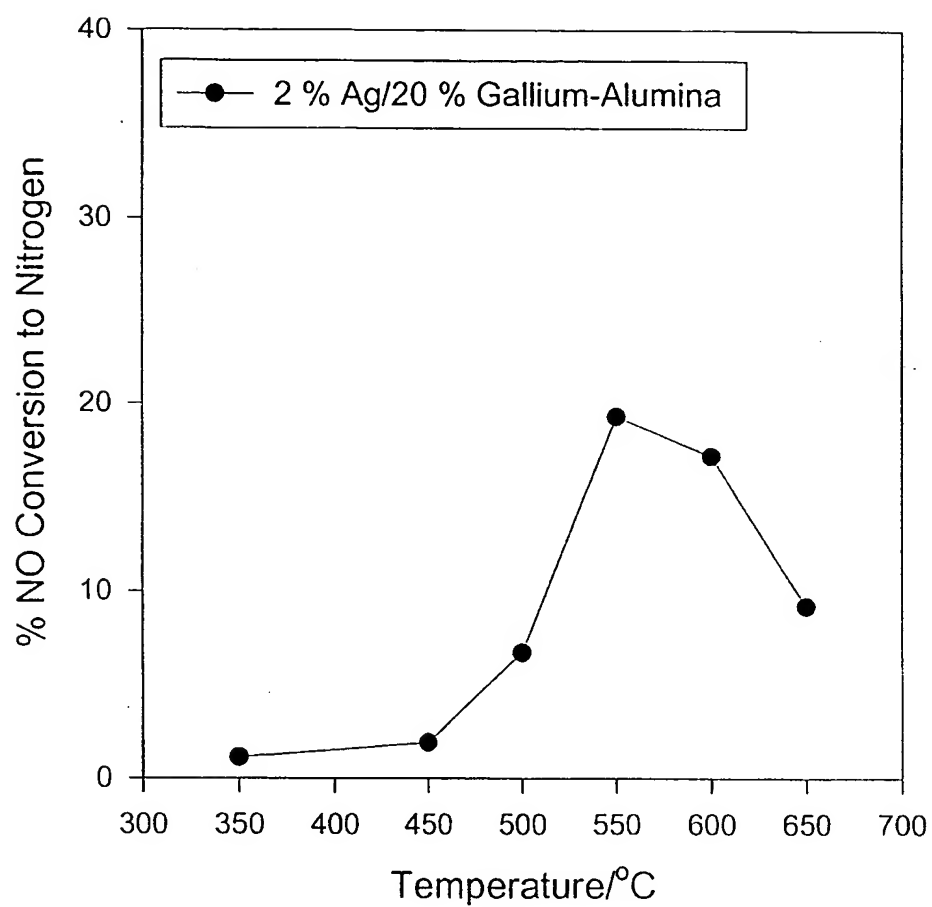


Fig. 16

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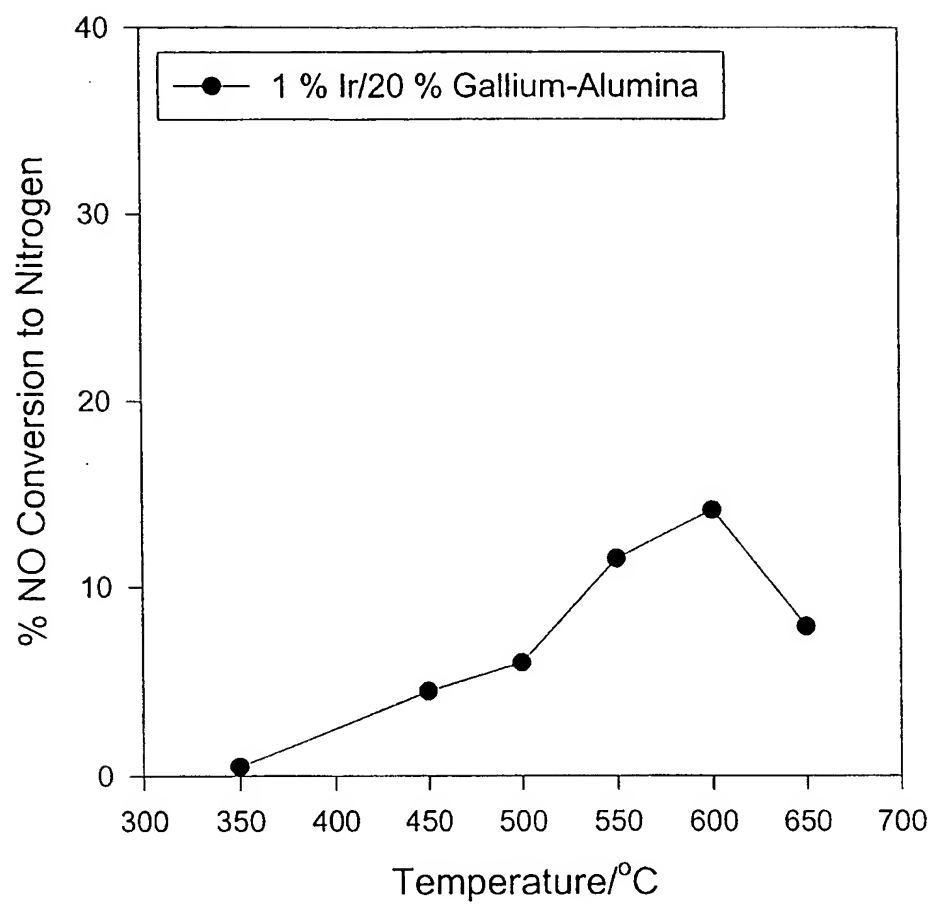


Fig. 17

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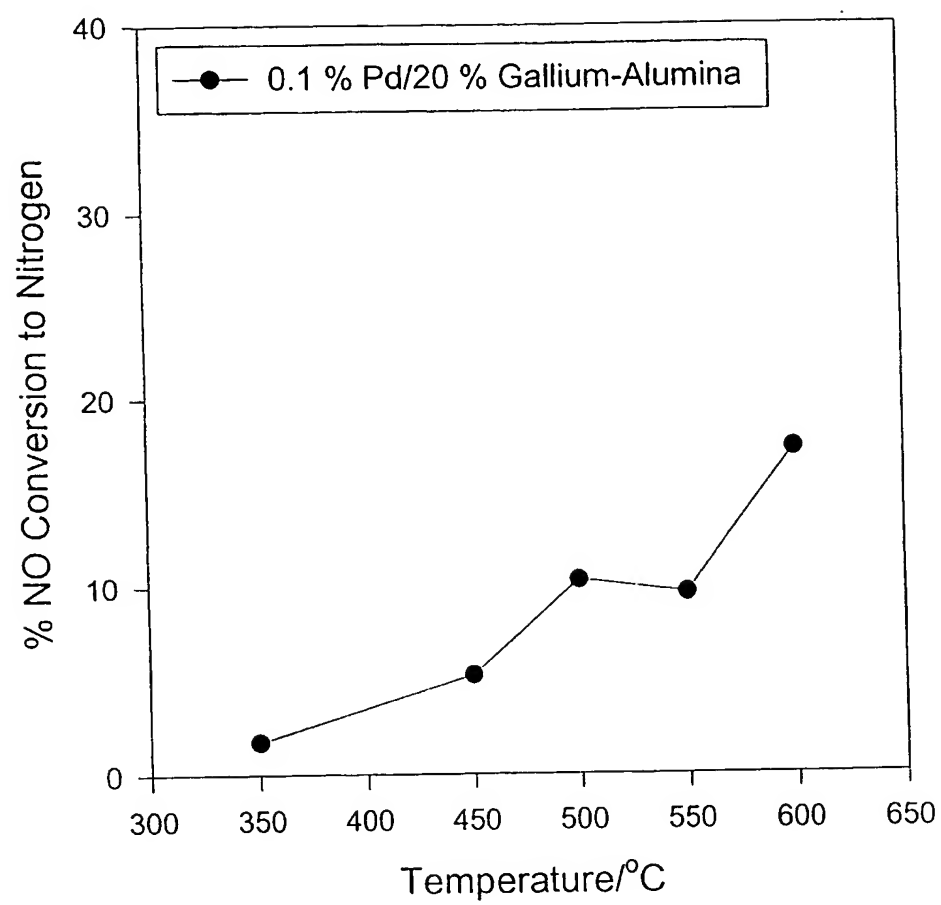


Fig. 18

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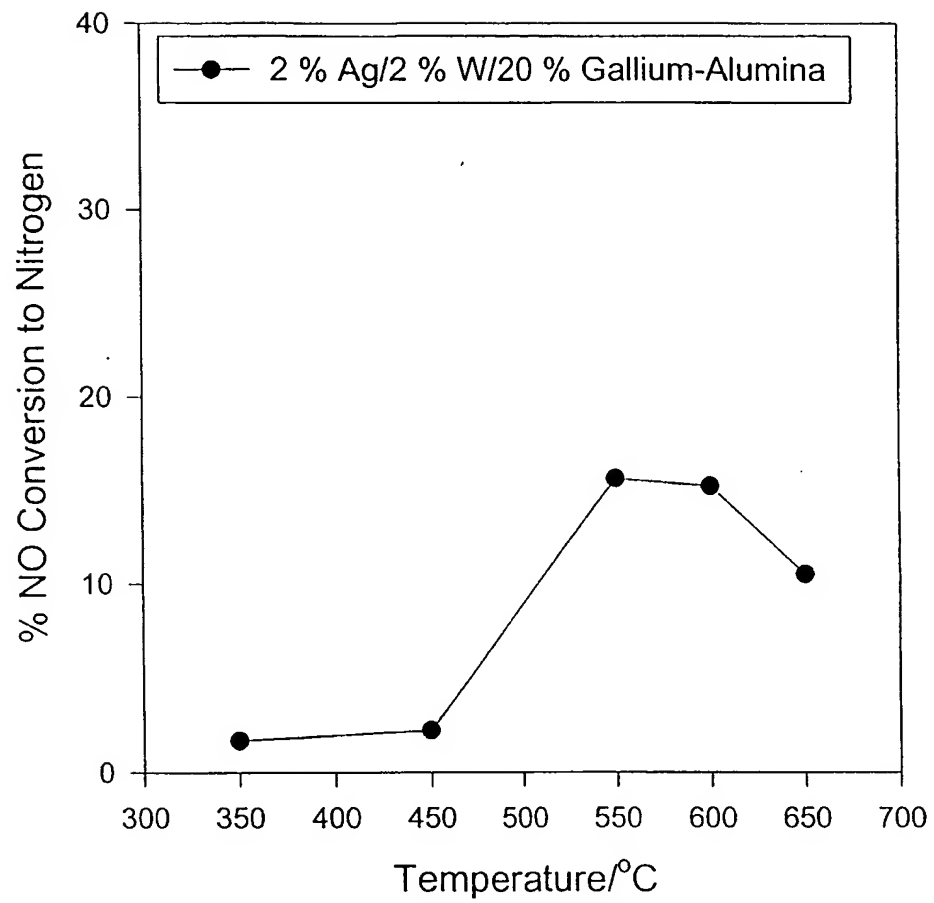


Fig. 19



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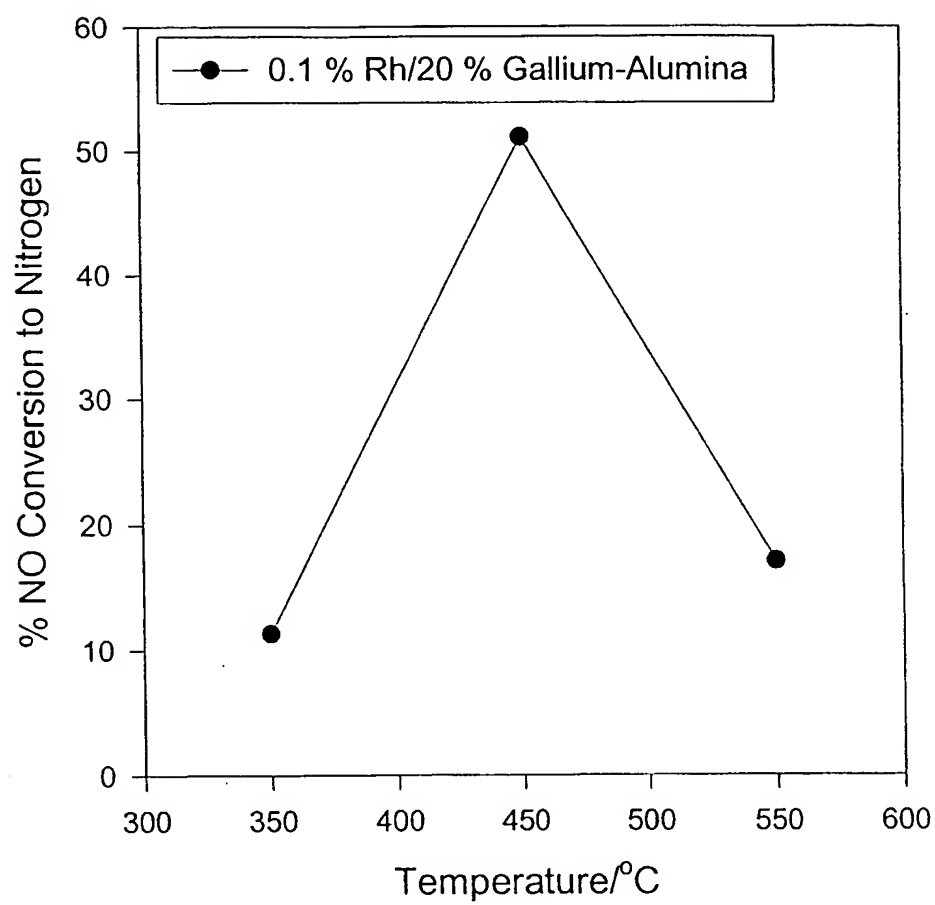


Fig. 20

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/AU00/00268

<b>A. CLASSIFICATION OF SUBJECT MATTER</b>												
Int. Cl. <sup>7</sup> : B01D 021/02, 021/04, 023/08; B01J 053/56, 053/86												
According to International Patent Classification (IPC) or to both national classification and IPC												
<b>B. FIELDS SEARCHED</b>												
Minimum documentation searched (classification system followed by classification symbols) B01D 021/02, 021/04, 023/08; B01J 053/56, 053/86												
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched AU:IPC as above												
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) WPAT: alumin+ and (gallium or boron or B or Ga) and nitr+												
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>												
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.										
X	US 5683572 A (Nakagawa) 4 November 1997, see whole document	1-23, 28										
X,P	US 5955046 A (Okimura et al.) 21 September 1999, see whole document	1-6, 11-13, 15-17, 19-28										
X	EP 696470 A (Mitsubishi Jukogyo KK) 14 February 1996, see whole document	1-6, 11-13, 15-17, 19-23, 28										
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C <input checked="" type="checkbox"/> See patent family annex												
<p>* Special categories of cited documents:</p> <table border="0"> <tr> <td>"A" document defining the general state of the art which is not considered to be of particular relevance</td> <td>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</td> </tr> <tr> <td>"E" earlier application or patent but published on or after the international filing date</td> <td>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</td> </tr> <tr> <td>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</td> <td>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</td> </tr> <tr> <td>"O" document referring to an oral disclosure, use, exhibition or other means</td> <td>"&amp;" document member of the same patent family</td> </tr> <tr> <td>"P" document published prior to the international filing date but later than the priority date claimed</td> <td></td> </tr> </table>			"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention	"E" earlier application or patent but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone	"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art	"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family	"P" document published prior to the international filing date but later than the priority date claimed	
"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention											
"E" earlier application or patent but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone											
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art											
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family											
"P" document published prior to the international filing date but later than the priority date claimed												
Date of the actual completion of the international search 27 April 2000		Date of mailing of the international search report - 3 MAY 2000										
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustalia.gov.au Facsimile No. (02) 6285 3929		Authorized officer  JOHN DEUIS Telephone No : (02) 6283 2146										

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU00/00268

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3980584 A (Dronov et al.) 14 September 1976, see whole document	1-4, 9-11, 19-23
X	Derwent Abstract Accession No. 96-459657/46, Class E36 H06 J04 (J01), JP 08229401 A (KYOCERA CORP) 10 September 1996	1-6, 11-13, 15-17, 19-23, 28
X	Derwent Abstract Accession No. 99-161718/14, Class E36 H06 J04 (J01), JP 11019513 A (AGENCY OF IND SCI & TECHNOLOGY) 26 January 1999	1-6, 11-13, 15-17, 19-23, 28
X	Derwent Abstract Accession No. 95-158050/21, Class E36 J01 (J04), JP 07080300 A (KYOCERA CORP) 28 March 1995	1-6, 11-13, 15-17, 19-23, 28
X	Derwent Abstract Accession No. 94-268789/33, Class E36 H06 J04, JP 06198172 A (AGENCY OF IND SCI & TECHNOLOGY) 19 July 1994	1-6, 11-13, 15-17, 19-23, 28
X	Derwent Abstract Accession No. 99-161717/14, Class E36 H06 J04 (J01), JP 11019512 A (AGENCY OF IND SCI & TECHNOLOGY) 26 January 1999	1-6, 11-13, 15-17, 19-23, 28

**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

International application No.  
**PCT/AU00/00268**

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report				Patent Family Member			
US	5683572	AU	10202/97	BR	9611847	CA	2238059
		CN	1203565	EP	863844	US	5580540
		WO	9720769	US	5911968		
US	5955046	JP	10151346				
EP	696470	JP	8052365	US	5710084	US	5972821
US	3980584	NONE					
JP	229401/8	JP	8229401				
JP	019513/11	JP	11019513				
JP	229401/8	JP	8229401				
JP	019513/11	JP	11019513				
JP	080300/7	JP	7080300				
JP	198172/6	JP	6198172				
JP	019512/11	JP	11019512				
END OF ANNEX							